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SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON CADMIUM

NATIONAL ENVIRONMENTAL RESEARCH CENTER

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March 1975

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SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON CADMIUM

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16. ABSTRACT

This report is a review and evaluation of the current knowledge of cadmium in the environment as related to possible deleterious effects on human health and welfare. Sources, distribution, measurement, and control technology are also considered. Cadmium is widely distributed in the environment. The air over urban areas has contained generally less than 0.1 microgram per cubic meter ($\mu g/m^3$), 24-hour average, but a 24-hour average as high as 0.73 $\mu g/m^3$ has been measured in the air of a community with a known cadmium source. The cadmium content of water generally is less than 1 part per billion although much higher values have been found. The cadmium content in foods varies widely. The estimated intake from foods is 25 to 75 micrograms per day. The human body burden of cadmium is cumulative. The half-time of cadmium in man is estimated at over 10 years. Man's primary exposure is from food, tobacco smoke, water, and ambient air. Food and tobacco smoke are the major sources except in the immediate vicinity of major sources of atmospheric emissions of cadmium. Emphysema and other lung diseases have been related to industrial exposure to airborne cadmium compounds. Kidney damage has also resulted from long-term exposure to cadmium. Animal experiments link anemia, hypertension, testicular necrosis, and carcinogenesis with cadmium exposure. Current knowledge of the dose-response relationship does not provide criteria on which to base standards.

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PREFACE

Although this report is issued in the Scientific and Technical Assessment Report Series, it differs in several respects from the comprehensive multi-media format that the Series will usually have because it was nearly completed prior to the creation of the STAR series in August 1974.

This document was prepared by a task force convened at the direction of Dr. John F. Finklea, Director, U.S. Environmental Protection Agency (EPA), National Environmental Research Center (NERC) at Research Triangle Park (RTP), N. C. Assembly, integration, and production of the report were directed by the Special Studies Staff, NERC-RTP. The objective of the task force was to review and evaluate the current knowledge of cadmium in the environment, especially in the atmosphere, as related to possible deleterious effects upon human health and welfare. Information from the literature and other sources has been considered generally through January 1973.

The primary reference for this report was *Cadmium in the Environment* (Publication Number EPA-R2-73-190), a review on cadmium performed under a contract agreement between the U. S. Environmental Protection Agency and the Department of Environmental Hygiene of the Karolinska Institute, Stockholm, Sweden.

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Review copies of this document also have been provided to other governmental agencies and to industrial and public interest groups.

All comments and criticisms have been reviewed and incorporated in the document where deemed appropriate.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
acfm	Actual cubic feet per minute
AFS	Atomic fluorescence spectroscopy
ASV	Anodic stripping voltametry
°C	Degrees Celsius
CD	Colorimetric dithizone
EPA	United States Environmental Protection Agency
°F	Degrees Fahrenheit
km	Kilometer

l	Liter
lb/ton	Pounds per ton
M	Molar concentration
m	Meter
m^3	Cubic meters
mg	Milligrams
mg/m^3	Milligrams per cubic meter
min	Minutes
$min\text{-}mg/m^3$ or $mg/m^3\text{-}min$	Time-concentration exposure or Exposure time in minutes times concentration in mg/m^3
MT	Metric tons
μg	Micrograms
$\mu g/m^3$	Micrograms per cubic meter
$\mu g/ml$	Micrograms per milliliter
μm	Micrometer
NAA	Neutron activation analysis
NASN	National Air Surveillance Network
ng/m^3	Nanograms per cubic meter
OES	Optical emission spectroscopy
ppb	Parts per billion
ppm	Parts per million

LIST OF CHEMICAL ELEMENTS AND COMPOUNDS

$B_2O_4^{2-}$	Metaborate
Cd	Cadmium
^{115}Cd	Cadmium isotope having atomic weight of 115
$CdCO_3$	Cadmium carbonate
CdS	Cadmium sulfide
CO_3^{2-}	Carbonate
CdO	Cadmium oxide
CdSe	Cadmium selenide
$CdSO_4$	Cadmium sulfate
$CuFeS_2$	Copper-iron sulfide (chalcopyrite)
HCO_3^-	Bicarbonate radical
H_2O	Water
PbS	Lead sulfide
SiO_3^{2-}	Silicate
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
$ZnCO_3$	Zinc carbonate
ZnO	Zinc oxide
ZnS	Zinc sulfide
Zn_2SiO_4	Zinc silicate (willemite)
$Zn_4Si_2O_7(OH)_2$	Basic zinc silicate (hemimorphite)
$ZnSO_4$	Zinc sulfate

SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON CADMIUM

1. INTRODUCTION

The purpose of this document is to summarize the current knowledge on cadmium in relation to its effect upon human health and welfare. *Cadmium in the Environment*[1] served as a basic reference for the review; however, the results of later studies and contributions from EPA staff members have been incorporated. The references cited do not constitute a comprehensive bibliography on the subject.

Our knowledge concerning the cycling of cadmium in the environment is incomplete. Because the principal human intake routes include food, water, and air, and because the half-time of cadmium in the human body is very long, any assessment of effects should consider the environmental cycle. The atmosphere may serve as a medium through which cadmium enters the soil and water, and hence the food chain. This document makes no attempt to treat this aspect of the subject in detail, but it recognizes the possible impact upon decisions concerning control strategies.

Each of the major human intake routes for cadmium is reviewed. Where justified by available evidence, estimates have been made of normal and "critical" intake levels.

1.1 REFERENCE FOR SECTION 1

1. Friberg, L., M. Piscator, G. Nordberg, and T. Kjellstrom. Cadmium in the Environment, II. The Karolinska Institute, Stockholm, Sweden. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C., under Contract No. 68-02-0342. Publication No. EPA-R2-73-190. February 1973. 169 p.

2. SUMMARY AND CONCLUSIONS

2.1 SUMMARY

Cadmium is widely distributed in the environment in trace amounts. Concentrations exceeding fractions of a part per million occur only in areas of rich ore deposits or in areas contaminated by man's activities.

Cadmium emitted into the atmosphere will generally be in the form of particles – usually as the oxide, but also as sulfide or sulfate. The primary man-made sources of cadmium released to the environment are metallurgical processing, reprocessing of materials, incineration or other disposal processes, and consumptive uses.

Because the boiling point of cadmium is quite low (767°C), the metal may be vaporized in high-temperature processes and condensed into particles as the process off-gases are cooled. This condensation would result in fine particulate matter, primarily in the micrometer and submicrometer range. The exact size distribution of cadmium-containing particles from these sources has not been clearly defined. Available data indicate that approximately 40 percent of the mass is in particles smaller than 2 micrometers in diameter; hence, a large portion of the particles would be in the respirable range.

Evidence indicates that a considerable mass of cadmium-containing particles is deposited on the surface of the earth at relatively short distances from the emission source – the maximum gradient is from 0 to 1 kilometer (0 to 0.6 mile), suggesting that large particles are also emitted. The submicrometer particles, however, would be transported greater distances – detectable gradients up to 100 kilometers (60 miles) have been reported.

In 1969, atmospheric concentrations of cadmium at 29 nonurban stations in the U. S. were below the minimum detectable level of 0.003 microgram per cubic meter ($\mu g/m^3$). Cadmium is present in small but measurable amounts in the air over almost all urban areas sampled by the National Air Surveillance Network of EPA. Higher annual average concentrations of cadmium are found in the small-to-medium size cities with heavy industry than in the most populous areas. The highest 24-hour, quarterly, and annual values – 0.73, 0.15, and 0.12 $\mu g/m^3$, respectively – were found in El Paso, Texas, where a known cadmium source is located. Average 24-hour concentrations of cadmium in urban areas are generally less than 0.1 $\mu g/m^3$. In the immediate vicinity of major emission sources, average 24-hour concentrations may reach 5 to 6 $\mu g/m^3$. Annual averages of 0.3 $\mu g/m^3$ have been reported in Sweden.

The cadmium content of surface water is normally less than 1 part per billion (ppb). However, a concentration of 77 ppb has been found in hot, running tap water, which was attributed to cadmium in the water pipe.

Cadmium values reported in foods vary widely; however, the accuracy of many of the values are questionable because of the analytical methods used. Values range from below detectable levels to several parts per million (ppm), depending upon the type of food and the degree of contamination. The varying ability of different species of plants to concentrate cadmium has not been explained. Tobacco, for example, has been found to contain a high concentration of cadmium. The uptake of cadmium by wheat has been related to the mount of cadmium added to the soil; however, the rate of uptake may be influenced by the presence of other elements or compounds. Fertilization and harvest practices are suspected of contributing

to the cadmium content in food; however, the relationship has not been conclusively demonstrated. The role of the atmosphere in the transport of cadmium, with subsequent deposition on the soil, is not understood. The majority of food consumed in the United States is grown in areas remote from primary cadmium emission sources.

Large doses of cadmium are known to be toxic. Some deaths have been reported as a result of exposure to high concentrations of cadmium oxide fumes. Acute pulmonary edema or proliferative interstitial pneumonitis may result from an acute exposure; the dose of cadmium necessary to produce such reactions has been calculated to be approximately 2,500 minutes-milligrams per cubic meter (min-mg/m^3). (This could, for example, represent an exposure to 100 mg/m^3 for 25 minutes, or to 50 mg/m^3 for 50 minutes).

Friberg found emphysema of the lung among male workers chronically exposed to cadmium oxide dusts in an alkaline accumulator factory in Sweden. Quantitative data concerning the exposure levels were incomplete; however, a range of 3 to 15 mg/m^3 was reported. Several other incidents of lung damage caused by cadmium exposure have been reported. Little information is available, however, concerning the possible association between respiratory diseases and exposure to cadmium via ambient air. Dose-response relationships cannot be established at the present time because time-weighted average exposures are available for only short periods of time.

In fatal cases of acute cadmium poisoning via inhalation, pathological changes have been found in the kidneys. The relationship between the dose of cadmium and the degree of kidney damage is poorly defined, however.

Microscopic changes have been reported in the livers of workers suffering from acute cadmium poisoning as a result of exposure to cadmium oxide fumes. Whether these changes represent a direct toxic effect of cadmium on the liver or whether they are merely secondary to cadmium-induced pulmonary edema is not known.

Long-term exposure to cadmium may cause renal tubular damage; "tubular proteinuria" is a major sign of this damage. The critical concentration of cadmium that may cause renal tubular dysfunction has been estimated to be 200 ppm in the renal cortex.

Evidence from animal experiments suggests a relationship between cadmium exposure and anemia, hypertension, testicular necrosis, and carcinogenesis; however, the evidence is not conclusive, and dose-response relationships have not been established in humans. Studies have shown that the addition of zinc, selenium, and sulfhydryl compounds may influence the effects of cadmium.

The body burden of cadmium is cumulative. The biological half-time is very long–over 10 years. Absorbed cadmium is stored mainly in the liver and kidney. The total body burden at age 50 varies considerably – 15 to 30 mg for people in some European countries and the United States; 50 to 60 mg in nonpolluted areas of Japan. The mean cadmium concentrations in renal cortex at age 50 is reported as 25 to 50 ppm in some European countries and the United States and 125 ppm in Tokyo. A critical level for the renal cortex is estimated at 200 ppm.

Minimum detectable health effects have been theoretically associated with long-term (25 to 30 years) exposure to air concentrations of 2.5 $\mu g/m^3$, or long-term daily dietary intake of 300 μg for the average man. The primary sources of cadmium intake for humans are food, tobacco smoke, water, and ambient air. The intake from breathing ambient air is small (about 1 percent) in comparison with food and tobacco, *except* in the immediate vicinity of point sources. Present estimates for some European countries, the United States, and Japan indicate that populations in areas not polluted by cadmium have a daily intake of cadmium from food of 25 to 75 μg. It has been calculated that, with an absorption of 5 percent of ingested cadmium, the daily intake would have to be 88 μg to reach the 50 ppm level in renal cortex in 50 years. To reach the 200 ppm level, approximately 300 μg would be required. Considerably less intake via food would be required for smokers and those living in the immediate vicinity of primary emission sources. Higher absorption rates may be found for individuals with calcium deficiency.

2.2 CONCLUSIONS

Many uncertainties remain regarding the cycling of cadmium, the contribution of man's activities to the redistribution of cadmium in the environment, and the effects upon human health and welfare. However, a number of conclusions can be made, albeit some of these may best be classified as tentative.

- Cadmium has a long biological half-time, and its toxicity is high. Chronic effects may result from long-term exposures to lower concentrations. The evidence suggests that cadmium may act as a carcinogen in man, but it is not conclusive.

- Of the three most important exposure routes for cadmium, exposure via breathing ambient air is the least significant, *except* in the vicinity of point sources. The major route is via food intake. Smoking may be an additional means of exposure.

- Transfer mechanisms whereby cadmium enters food chains are not adequately described.

- Detailed information on absorption factors, biological half-time, renal concentrations, and total body burden as related to acute and chronic health effects is lacking.

- Atmospheric concentrations approaching a "critical exposure" level may occur in the immediate vicinity of point sources.

- In general, current ambient atmospheric concentrations of cadmium do not pose a direct threat to the health and welfare of the general population; however, certain practices such as disposal of plastics and other materials containing significant amounts of cadmium by incineration may tend to make the pollutant more ubiquitous.

- Any action in pollution control that reduces particulate matter emissions will reduce the potential exposure to airborne cadmium; however, the degree of control with current technology is not known. Current technology is inadequate for capturing very fine particles.

- Not enough is known regarding the cycling of cadmium and dose-response relationships to specify the degree of control required.

- The atmospheric transport of cadmium from primary emission sources, with subsequent deposition, will contribute to cadmium contamination of soil; however, the degree to which this mechanism contributes to cadmium in the general food supply of the United States is unknown. Evidence suggests that fertilizing and harvesting practices may be more important factors than atmospheric transport.

3. CHEMICAL AND PHYSICAL PROPERTIES

Cadmium is chemical element number 48 and has an atomic weight of,112.40. It melts at 320.9°C and boils at 767°C. Two and zero are its only stable valences.

The saturation vapor pressure of cadmium is so low that at room temperature less than 1 nanogram of cadmium per cubic meter of air (1 ng/m^3) is in tine vapor phase when the metal and the atmosphere are in equilibrium.[1]

Cadmium is a bluish-silver metal which retains its metallic luster even after tarnishing in the air. It is ductile and easily worked.[1,2]

Cadmium is more chemically reactive than mercury, which is below it on the atomic table, and less reactive than zinc, which is above it. It is, therefore, intermediate in its behavior between mercury and zinc.[3] It readily forms alloys with a majority of the heavy metals. It also forms a number of salts, the most common of which is cadmium sulfate. Cadmium sulfate is soluble in both cold and hot water.[1]

3.1 REFERENCES FOR SECTION 3

1. Handbook of Chemistry and Physics, 53rd Ed. Cleveland, Chemical Rubber Co., 1972. p. D-56;

2. Mineral Facts and Problems, 1970 Ed. U. S. Department of Interior, Bureau of Mines, Washington, D. C. Bulletin No. 650. 1970.

3. Cadmium: The Dissipated Element. Fulkerson, W. and H. E. Goeller (Ed.). Oak Ridge National Laboratory, Oak Ridge, Tenn. 1973.

4. SAMPLING, PREPARATION, AND ANALYSIS

The two major factors essential to obtaining reliable emission data are sampling procedures that provide quantitatively representative samples of the pollutant emissions and analytical methods that meet the requirements for sensitivity, accuracy, and precision. By contract, EPA has reviewed sampling and analytical procedures for cadmium and developed a tentative procedure for sampling cadmium from stationary sources. The methods discussed below are based on an evaluation of available technical literature but should be subjected to laboratory and field testing, with modification where necessary.

4.1 SAMPLING PROCEDURES

The problem of collecting representative samples is complicated by the multitude of source configurations that exist. Cadmium is emitted from both stack and diffuse sources. Because stacks constitute a relatively well-defined source configuration, the possibility of obtaining reliable stack emission data is much better than in the case of diffuse sources. For stack sources, EPA recommends a sampling train consisting of probe, filter holder, impingers, and associated metering system for isokinetic sampling. The volume flow rate of stack effluents also must be obtained in order to derive pollutant mass emission rates. For diffuse sources, accurate emission data are virtually impossible to obtain by methods currently employed. The usual practice is to do sampling and analysis for ambient concentrations in the vicinity of such sources and to use such data in conjunction with estimated rates of thermal diffusion, turbulent diffusion, deposition, etc. to derive approximate emission rates.

Except in the case of continuous monitors, it is most convenient to consider environmental sampling and analysis separately. Generally, the method of analysis is independent of the origin of the sample, with procedural differences consisting of variations in methods of sample preparation.

4.1.1 Air

Samples are taken from ambient air by filtration through porous media of low, known cadmium content such as glass-fiber filters or membrane filters. The filter is held by a flexible gasket in a holder that is a part of a device made to exclude debris, facilitate maintenance, regulate the time of sampling, and permit estimation of the air volume. The sample of particulate matter so collected is prepared for subsequent analysis by combustion (use of a low-temperature asher will eliminate loss of cadmium by volatilization) and dissolution of cadmium in the residue by use of acids.[2,3] Wet digestion with acids is also a reliable technique.

4.1.2 Water

Water may be sampled by continuous withdrawal of a sample from a pipe or stream, but the more common method is batch sampling. Clean, acid-washed borosilicate containers should be used, and the samples analyzed as soon as possible. When only one set of samples is to be taken from a stream or lake, it is best to sample at the middle depth. Cadmium can be lost from solution in trace quantities by absorption on container walls, even those made of resistant glass.

4.1.3 Soil

Soil samples for cadmium are taken using a systematic method such as sampling at points on a grid plotted to cover the area of interest. In general, a soil sample obtained from the top 12 inches is thoroughly mixed

and reduced to a size suitable for analysis by using a riffle or the cone and quarter method; both reduce the sample by discarding a portion in each operation. The sample is then ashed (preferably at low temperature), and the cadmium is extracted with mineral acids of low cadmium content.

4.1.4 Food

Food samples may be taken as "market basket" samples, which are obtained from normal supply channels in the proportions representative of an average diet. Market basket survey samples are probably the best index of average human ingestion. When the intake of individuals is surveyed, a fixed proportion of each dish to be consumed by an individual is placed in a sample container for subsequent analysis. Food samples are ashed at low temperature, and the residue is extracted with acid to yield a solution suitable for analysis.

4.2 ANALYTICAL METHODS

Methods available for analysis of collected cadmium emission samples include atomic absorption, atomic fluorescence, anodic stripping voltametry, ultraviolet and visible spectroscopy, polarographic procedures, and titrimetric analysis. Multielemental techniques sometimes used are spark-source mass spectrography and optical emission spectrography. X-ray fluorescence appears promising as a rapid, accurate, nondestructive, multielemental technique.

In general, the analytical methodology employed is determined by resource considerations and how the data are to be used. Potentially, any method of analysis capable of determining cadmium in the concentrations to be found in environmental samples should be acceptable, but in practice the number of methods in extensive use has been restricted to the classical procedures of colorimetric dithizone (CD), optical emission spectroscopy (OES), neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS), and anodic stripping voltametry (ASV). The dithizone method consists of the formation of a colored dithizone cadmium complex, separation of interferents by closely controlled multiple extractions with various reagents, spectrophotometric determination of the colored complex, and estimation by reference to known responses. The CD method is slow, tedious, and requires excellent technique, but gives reliable results.

The OES procedure uses expensive instrumentation and consists of exciting the cadmium atoms in a sample by electric arc or spark, separation of the emitted light that is characteristic of cadmium by means of a prism or grating, elimination of other lines by means of selective slits, and measuring the light intensity on film or by phototube. The line intensity is compared with the response from standards, and the cadmium content is estimated. The film approach is semiquantitative, whereas the photometric procedure is more quantitative.

The NAA approach involves irradiation of a sample with neutrons. Cadmium is detected by identification of the radiation emitted by activated cadmium atoms; chemical separation may be necessary to remove interferents. NAA costs, comparatively, are very high, but the sensitivity is good, and the accuracy compares favorably with that of OES.

The AAS procedure consists of exciting vaporized sample atoms in a flame positioned in the path of light from a lamp that has a cathode made of the metal of interest – cadmium in this case. The cadmium atoms in the ground state in the beam will absorb this characteristic radiation. The attenuation of light by the sample is compared with that caused by known cadmium standards, and the cadmium content of the sample is estimated. Using a deuterium background corrector, atomic absorption spectroscopy meets the requirements for sensitivity, accuracy, precision, ease of handling, speed, and relatively low-cost equipment. AAS is the most frequently used analytical method and is rapidly becoming the accepted method to determine cadmium at trace levels. The sensitivity of AAS can be increased by using dithizone as a chelating agent[1] or by using a heated graphite atomizer.

Interferences in the analysis of cadmium by AAS have been reported[3] to be caused by anions such as $B_2O_4^{-2}$, $S_1O_3^{-2}$, CO_3^{-2}, and HCO_3^{-}. Phosphate in concentrations above 0.1 molar (M) could decrease the absorption, and sodium chloride above 0.01M could increase absorption. These interferences can be removed, if necessary, by extraction of the cadmium into an organic solvent before analysis.

The ASV method consists of measuring the current flow per unit time at varying voltages, which are characteristic of the deposition of metals. Most of the cadmium experience with ASV has been with blood samples for which rapid, cheap, accurate results are claimed.

Atomic fluorescence spectroscopy has high sensitivity, but this method should be held in reserve until it is more widely accepted.

4.2.1 Air

Cadmium in air can be estimated continuously by using an excitation source consisting of graphite rods energized by induction with a radio-frequency coil. At present, the sensitivity of the procedure does not permit ambient air analysis, and the equipment is too bulky and complex to be portable. The method in general use consists of examination of a solution obtained by processing a particulate matter sample on a filter of glass fiber or organic membrane. The detection is by OES when a multi-element survey is required: AAS is used when cadmium values alone or data of high accuracy are desired.

In the National Air Surveillance Network, particulate matter samples are sectioned, and composites are ashed in a low-temperature asher using 50 to 100 milliliters (ml) of oxygen per minute at 1 torr[2] with an induction coil energized with 250 watts. At this combustion temperature (about 150°C) cadmium is retained essentially quantitatively, whereas half of the cadmium in samples oxidized in a muffle furnace is lost at between 500 and 550°C.[1] The residue is extracted using a mixture (4:1 by volume) of redistilled nitric and hydrochloric acid and concentrated. The solution is then freed of silica by centrifugation and brought up to volume with redistilled nitric acid. The solution is analyzed directly by OES, which has a detection limit of 0.3 microgram per milliliter (μg/ml) of sample and a relative standard deviation of 8 percent at 0.8 μg/ml. For special studies, this solution is diluted 10:1 with water prior to analysis by AAS. The minimum level detectable by AAS is 0.04 μg/ml, and the standard relative deviation is 2 percent at or above 0.5 μg/ml.

4.2.2 Water

Water samples are best analyzed directly by AAS, using the graphite furnace technique. If interferents are expected, the samples may be taken to dryness, and the residue digested with nitric acid. If the cadmium concentration is not detectable, evaporation or extraction with a chelating agent and organic solvent will serve to concentrate the cadmium in the solution analyzed. Friberg et al.[4] describe measurement of cadmium in water very well.

4.2.3 Soil

Soil samples, prepared for analysis by oxidation and acid extraction, can be analyzed for cadmium by suitable techniques; AAS is the usual method of choice.

4.3 REFERENCES FOR SECTION 4

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5. ENVIRONMENTAL APPRAISAL

5.1 ORIGIN AND ABUNDANCE

5.1.1 Natural Sources

Cadmium, a relatively rare metal with an estimated abundance in the earth's crust of 0.55 gram per metric ton, is *always* found in nature in association with zinc. It varies from 0.1 to 5 percent of the amount of zinc present in zinc and polymetallic ores.[1] Table 5.1 shows both the average terrestrial abundance and the amounts in different types of rocks, soils, and sea water. The ratio of cadmium to zinc is based on 55 ppm for the continental abundance of zinc and 0.15 ppm for cadmium. The continental abundance is based on rocks that are predominantly granitic and contain larger amounts of cadmium.[2]

Table 5.1. DATA ON NATURAL ABUNDANCE OF ZINC AND CADMIUM[2]

Type source	Abundance, ppm		Specific zinc/ average zinc[a]	Cd/Zn, %
	Zinc	Cadmium		
Worldwide	80	0.18	1.46	0.23
Continental	55	0.15	1.00	0.27
		0.5[3,4]		
Ultramatic rocks	150	0.0	2.73	
Basaltic rocks	112	0.22	2.04	0.20
High-calcium granites	47	0.13	0.85	0.28
Low-calcium granites	39	0.13	0.71	0.33
Syenitic rocks	26	0.13	0.47	0.50
Avg. igneous rocks	70	0.2	1.27	0.27
Shales	45-95	0.3	0.82-1.72	0.67-0.32
Sandstone	16	0.05	0.29	0.31
Limestone	20	0.035	0.36	0.17
Soil				
Range	10-300	0.01-0.7	0.2-5.4	0.1-0.23
Average	50	0.06	0.9	0.12
Seawater[5]	0.01	0.0001		1.0

[a]Abundance for specific rock type/continental abundance.

Assuming these two abundance values, the topmost 2 kilometers of the continental lithosphere contain on the order of 40 trillion tons of zinc and 100 to 200 billion tons of cadmium. All of the oceans contain roughly 15 billion tons of zinc and 150 million tons of cadmium.[2] Economically, it is possible to recover only small amounts of these reserves. Known U. S. and world reserves and potential resources of zinc and cadmium are given in Table 5.2.

Table 5.2. TOTAL AND RECOVERABLE RESERVES AND RESOURCES OF ZINC AND CADMIUM IN THE U.S. AND THE WORLD[2] (10^3 MT)

	Total in resources		Recoverable[a]	
	U. S.	World	U. S.	World
Zinc				
Reserves, measured and indicated	15,500	112,000	12,000	86,000
Reserves, inferred	15,100	∿97,000	11,600	∿75,000
Total reserves	30,600	∿209,000	23,600	∿161,000
Potential resources	56,400	∿336,000	43,400	∿259,000
Total reserves and resources	87,000	∿545,000	67,000	∿420,000
Cadmium				
Reserves, measured and indicated	95	712	54	400
Reserves, inferred	91	∿730	51	∿410
Total reserves	186	∿1,442	105	∿810
Potential resources	∿195	∿1,800	∿105	∿1,020
Total reserves and resources	∿381	∿3,242	∿210	∿1,830

[a]Based on Bureau of Mines estimates of 77 percent of zinc and 56 percent of cadmium in ore; higher percentages, especially for zinc recovery in the U. S. (∿86 percent), are thought to be currently more appropriate.

Cadmium and zinc occur in ore deposits principally as sulfides. Ores in the eastern United States are purer zinc ores; those west of the Mississippi River are chiefly mixed sphalerite–galena-chalcopyrite (ZnS-PbS-$CuFeS_2$) ores.[2]

5.1.2 Man-made Sources

5.1.2.1 *Stationary Sources*–The principal industrial sources that release cadmium into the environment are the primary metals industry, including mining and processing; waste disposal by incineration; fertilizer processing; and the burning of fossil fuels. Metallic cadmium is prepared commercially as a by-product of primary metal industries, principally the zinc industry. Cadmium is found not only in zinc ore, but in lead, copper, and other ores that contain zinc minerals. During ore separation, cadmium remains with the zinc. Because the separation processes are not complete, lead concentrates will contain small amounts of zinc and smaller amounts of cadmium. The U. S. and world production of cadmium for the period 1964 to 1970 is shown in Table 5.3. The producers of zinc and cadmium in the United States are listed in Table 5.4.

Table 5.3. U. S. AND WORLD PRODUCTION OF CADMIUM, 1964 TO 1970[4] (10^3 kg)

Year	United States	World
1964	4,743	12,704
1965	4,387	11,907
1966	4,745	13,002
1967	3,946	12,827
1968	4,831	14,076
1969	5,736	17,049
1970	4,445	15,600

Table 5.4. SUMMARY OF U. S. ZINC AND CADMIUM PRODUCERS[4,5]

Rank in primary zinc output	Producer	Location	Primary cadmium producer
1	St. Joseph Lead Co.[a]	Josephtown, PA	X
		Herculaneum, MO	
2	New Jersey Zinc Co.[a]	Palmerton, PA	X
		Depue, IL	X
3	American Smelting & Refining Co.	Amarillo, T X	
		Corpus Christi, T X	X
		Selby, CA	
		El Paso, T X	
		Denver, CO	
		Beckenmeyer, IL	
		San Springs, OK	
		Trenton, NJ	
4	The Anaconda Co.	Anaconda, MT	
5	American Smelting & Refining Co.	Hillsboro, IL	
6	The Bunker Hill Co.	Kellog, ID	X
7	Blackwell Zinc Co.	Blackwell, OK	X
8	The Eagle Pitcher Co.[a]	Henryetta, OK	
		Galena, KS	X
9	National Zinc Co.	Bartlesville, OK	X
10	Athletic Smelting & Refining Co.	Fort Smith, AR	
11	International Smelting & Refining Co.	Tooele, UT	
	Sherwin Williams Co.	Coffeyville, KS	
	Apex Smelting Co.	Chicago, IL	
	Arco Die Cast Metals Co.	Detroit, MI	
	W. J. Bullock, Inc.	Fairfield, AL	
	General Smelting Co.	Bristol, PA	
	Gulf Reduction Co.	Houston, T X	
	H. Kramer Co.	El Segundo, CA	
	Pacific Smelting Co.	Torrance, CA	
	Sandoval Zinc Co.	Sandoval, IL	
	Superior Zinc Co.	Bristol, PA	
	Wheeling Steel Corp.	Martins Ferry, OH	
	Arkansas Metals Co.	Jonesboro, AR	
	United Refining & Smelting Co.	Chicago, IL	

[a]These companies also produce major quantities of zinc pigments and compounds directly from ore at eight plants.

Cadmium and zinc are released into the environment either through volatilization or through washing and solubilization. Volatilization occurs at quite low temperatures (cadmium 767°C and zinc 907°C) so that they are readily released by such thermal processes as ore roasting, pyrosmelting, steel scrap melting, incineration of wastes, and burning of fossil fuels.[2] Activities through which cadmium can be released to the air because of volatilization are listed in Table 5.5.

Table 5.5. OPERATING TEMPERATURES OF ACTIVITIES IN WHICH ZINC AND CADMIUM CAN BE RELEASED AS AIRBORNE POLLUTION[2]

Activity	Temperature		Approximate quantities, 1968, MT	
	°C	°F	Zinc	Cadmium
Galvanizing	425-460	790-850	435,000	(204)[a]
Rolled zinc, melting	445-510	840-950	45,000	(11)
Diecasting (2500 psi)	500	930	508,000	(16)
Silver solders	650	1,200		
Refuse incinerators	810	1,500		
Zinc ore roasting	920	1,600	1,000,000	5,900
Brass ingot making	1,000-1,100	1,830-2,000	295,000	(140)
Lead slag fuming	1,100-1,150	2,000-2,090	73,000	45
Zinc ore sintering	1,200	2,190	530,000	3,200
Zinc ore smelting	1,300	2,360	530,000	450
Lead blast furnace	1,400	2,550	∿73,000	∿45
Copper converting	1,200	2,200	<45,000	<180
Steel scrap melting	1,670-1,700	3,000-3,200	145,000	1,000

[a]Values in parentheses indicate approximate amounts of cadmium as impurities in zinc.

Release of cadmium from washing and solubilization occurs from overburden, tailing piles, and ponds at mines, slag heaps at smelters, residue piles at electrosmelters and refuse dumps, and from accidental releases from chemical and electroplating plants.[2] Estimates made by Davis and Associates[6] of the total annual emissions of cadmium to the atmosphere in the United States from major known source groups are shown in Table 5.6. Cadmium emissions to the atmosphere as the result of electroplating operations were estimated to be negligible. Another tabulation of cadmium emissions, prepared by the Standards Development and Implementation Division of EPA, is presented in Table 5.7. It should be clearly understood that these emission data are estimates and that efforts to obtain better information should continue.

Losses of cadmium to the environment at various stages in the societal flow of cadmium are poorly known. For this reason, the estimates given in Figure 5.1 are very crude.

Output of cadmium from incinerator sources may increase considerably because of rapid growth in the use of plastics. Cadmium compounds are used as stabilizers as well as pigments in plastics. It is difficult to estimate how much of a given compound is used industry-wide because of rapid changes in types and amount used. Although the cadmium concentration of phosphate rock processed into fertilizer varies from one source to another, it is usually greater than the natural abundance of the element.

More data are needed on the cadmium content in coal and other fuels to obtain a better assessment of cadmium release from the burning of fossil fuels. Coal combustion processes are potentially a significant source of cadmium emissions, but the magnitude of the emissions is not yet clearly defined. If the 454 million metric tons (MT) (500 million tons)[4] of bituminous coal burned in the United States during 1970 are assumed to have had a cadmium content of about 0.5 ppm, then the maximum possible cadmium emissions from combustion of this coal – assuming no controls – would be 245 MT (270 tons). This figure is over 10 percent of the total emissions from other sources listed in Table 5.6. The actual emissions of cadmium from coal combustion processes will depend upon the efficiency of cadmium removal by control

devices treating the off-gases from the processes. Device efficiency varies from source to source. Moreover, the stated efficiencies of devices in use apply to their efficiency in collecting total particulate matter; because a significant fraction of cadmium may be present in very fine particles that are difficult to collect, it is quite possible that the efficiency of these devices in removing cadmium may be well below the total design efficiency. It is clear, then, that total combustion may be a significant source of cadmium, but that additional investigation is required before a meaningful estimate can be made.

The principal uses of cadmium are as protective coatings (mainly by electroplating), as a paint pigment, as a plastic stabilizer, and in electrical storage batteries. Cadmium plating protects steel, iron, copper, and brass from corrosion. The estimated growth in demand projected by the Bureau of Mines[1] (Table 5.8) suggests that a large increase in the use of cadmium as a plastic additive will occur. Smaller quantities of cadmium are used as alloying agents, in fungicides, pesticides, nuclear control elements, photography, and cathode ray screens.

Table 5.6. ESTIMATED CADMIUM EMISSIONS TO THE ATMOSPHERE IN THE UNITED STATES, 1968[6]
(kilograms)

Source category	Estimated emissions
Mining	240
Metallurgical processing Cd separation from ores	950,000
Reprocessing	
Pigments	9,500
Plastics	3,000
Alloys	2,000
Batteries	200
Miscellaneous	500
	15,200
Consumptive uses	
Rubber tires	5,200
Motor oil	830
Fungicides	200
Fertilizers	410
	6,640
Incineration or other disposal processes	
Plated metal	900,000
Radiators	110,000
Other	86,000
	1,096,000
Total emissions	2,068,080

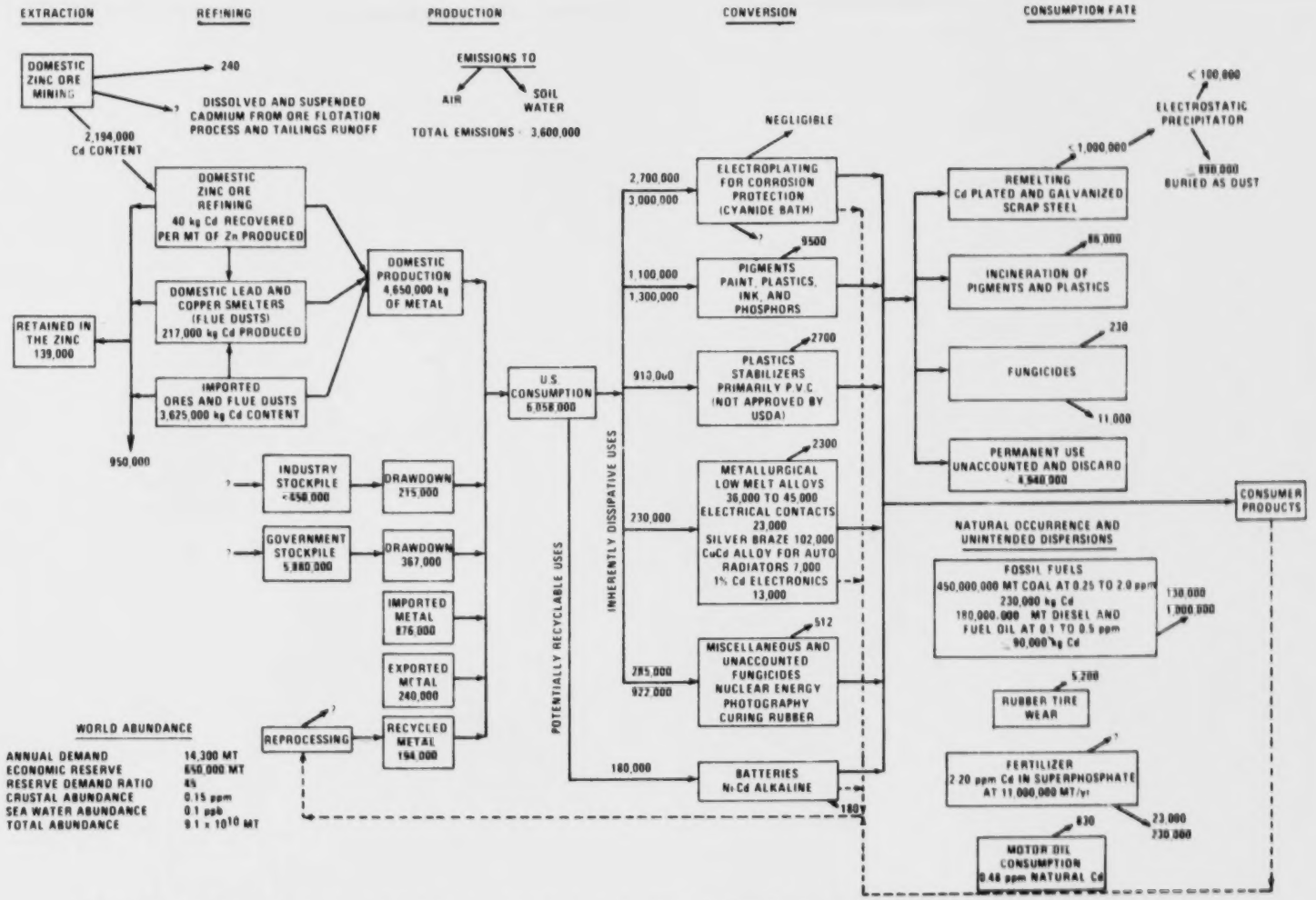

Figure 5.1. Flowsheet of societal flow of cadmium in U.S., 1968.[2] (Quantities in kilograms of metal unless indicated otherwise.)

Table 5.7. ESTIMATED U.S. EMISSION INVENTORY FOR CADMIUM, 1971

Source category/source	Estimated emissions, kg	Estimated emission factor[a]	Number of emitting facilities
Mining			
Mining	320	0.01 kg Cd/MT Cd mined	100
Primary metallurgical processing			
Zinc operations	584,200	155 kg Cd/MT Cd input	9
Lead smelting	148,000	490 kg Cd/MT Cd input	6
Copper smelting	212,000	900 kg Cd/MT Cd input	15
Cadmium units	54,400	15 kg Cd/MT Cd input	8
Metallurgical reprocessing			
Reclaiming of steel scrap	70,800	0.001 kg Cd/MT scrap	160
Secondary copper operations	59,000	2 kg Cd/MT auto radiators	<50
Secondary zinc operations	19,000	0.007 kg Cd/MT Zn produced	12
Reprocessing			
Plastic stabilizers	3,000	3 kg Cd/MT Cd charged	3
Pigments	6,400	8 kg Cd/MT Cd charged	8
Alloying	1,100	5 kg Cd/MT Cd charged	Unknown
Other	450	1 kg Cd/MT Cd charged	Unknown
Disposal			
Municipal incineration	44,000	500 kg Cd/MT Cd incinerated	197
Sewage sludge incineration	125,000	500 kg Cd/MT Cd incinerated	190
Other sources			
Consumption of coal[b]			
Coal-fired power plants	73,000	500 kg Cd/MT Cd burned	750
Coke ovens	34,000	750 kg Cd/MT Cd burned	65
Industrial and commercial boilers	18,000	500 kg Cd/MT Cd burned	Unknown
Consumption of diesel and heating oils	54,000	1000 kg Cd/MT Cd input	Mobile and unknown stationary
Consumption of rubber tires	5,170	100 kg Cd/MT Cd impurity	Mobile
Limited information sources			
Processing of phosphate rock			
Secondary cadmium recovery operations			
Consumption of gasoline			
Total estimated kg/year: stationary - 1,479,840; mobile - 32,000; combined - 1,511,840			

[a]Derived from emission factors in lb/ton by multiplying by 0.5 to convert to kilograms per metric ton.

[b]Based on 0.5 ppm cadmium content in coal and no control of emissions.

Table 5.8. ANTICIPATED GROWTH, BY USE, IN DEMAND FOR CADMIUM IN THE UNITED STATES, 1968-2000[1]

Application	1968		2000		% increase 1968-2000
	10^3 MT	% of total	10^3 MT	% of total	
Electroplating:					
Motor vehicles	0.59	9.8	2.04	14.9	245
Aircraft and boats	0.36	6.0	0.59	4.3	64
Other	2.68	44.4	4.50	32.8	68
Subtotal	3.63	60.2	7.13	52.0	96
Plastics	1.13	18.7	4.10	29.9	263
Pigments	0.68	11.3	1.13	8.2	66
Batteries	0.18	3.0	0.68	5.0	277
Other	0.42	6.9	0.68	5.0	62
Total	6.04	100	13.72	100	127

5.1.2.2 *Mobile Sources*–The available data concerning the emissions of cadmium directly from motor vehicles are limited. Jungers et al.[7] reported that the levels of cadmium in 22 samples of premium gasoline ranged from < 0.001 to 0.03 μg/ml. In 22 samples of regular gasoline, the cadmium concentration was less than 0.08 μg/ml; in six samples of low-lead gasoline, it was less than 0.04 μg/ml.[7] These values were obtained by the isotope dilution spark source mass spectrometry, an analytical technique that provides great precision and accuracy.

5.2 CONCENTRATIONS

5.2.1 Air

Cadmium emitted into the air from numerous and varied sources is associated with particles ranging from submicrometer to possibly 100 micrometers or greater in diameter. The retention time of these particles in the air depends on particle size, wind factors, and other physical and meteorological parameters. The smaller particles may remain suspended indefinitely, whereas the larger ones settle out immediately and are deposited on various surfaces. The greatest research effort has been expended on studies of suspended cadmium, although a number of investigations directed at cadmium deposition have been carried out.

5.2.1.1 *Cadmium in Suspended Particulate Matter*

5.2.1.1.1 *National Air Surveillance Network Studies*–Since 1957, ambient air concentrations of cadmium collected in suspended particulate matter samples at some 300 urban and 30 nonurban NASN sites distributed over the United States have been determined. Because of relatively low sensitivity, the spectrographic method of analysis was unable to determine the low ambient cadmium concentrations prevailing in the majority of cities. Thus, the data base is not adequate for determining the long-term trend for cadmium. In recent years, analytical methodology has been improved to the extent that data for a large number of sites are now available. The 1969 data representing the maximum number of NASN sites provide the most comprehensive base for demonstrating the distribution of cadmium in the atmosphere. The quarterly and annual average concentrations in the air of the 20 most populous cities are shown in Table 5.9. Table 5.10 provides the same kind of information, plus the percentage of cadmium in the particulate

Table 5.9. QUARTERLY AND ANNUAL AVERAGE CADMIUM CONCENTRATIONS[a] IN AIR OF THE 20 MOST POPULATED U.S. CITIES, 1969
($\mu g/m^3$)

City	Quarterly average				Annual average
	1	2	3	4	
New York City, NY	0.017	0.023	0.004	0.011	0.014
Chicago, IL	0.015	0.014	0.015	0.015	0.015
Los Angeles, CA	0.006	0.006	0.006	0.006	0.006
Philadelphia, PA	0.010	0.014	0.020	0.015	0.015
Detroit, MI	0.011	0.015	0.014	0.010	0.012
Houston, TX	<0.003[b]	0.005	0.005	0.005	0.004
Baltimore, MD	0.011	0.010	0.008	0.017	0.011
Dallas, TX	0.005	0.003	0.004	0.008	0.005
Washington, DC	0.010	0.006	0.007	0.008	0.008
Indianapolis, IN	0.005	0.020	0.025	0.011	0.015
Cleveland, OH	0.012	0.024	0.015	0.008	0.015
Milwaukee, WI	0.006	0.017	0.010	0.008	0.010
San Francisco, CA	0.005	<0.003	<0.003	0.006	c
San Diego, CA	0.007	0.012	0.015	0.006	0.010
San Antonio, TX	0.003	<0.003[b]	0.003	0.003	0.003
Boston, MA	0.007	0.008	0.005	0.004	0.006
Memphis, TN	0.003	0.004	0.003	0.005	0.004
St. Louis, MO	0.013	0.060	0.041	0.031	0.036
New Orleans, LA	0.004	0.004	0.005	0.004	0.004
Phoenix, AZ	0.005	0.005	0.005	0.009	0.006

[a]Minimum detectable concentration (MDC) = 0.003 $\mu g/m^3$.
[b]MDC/2 used for computation of annual averages.
[c]Insufficient data to permit computation.

matter for those cities with annual average concentrations greater than 0.015 $\mu g/m^3$. The quarterly values could reflect any seasonal differences that might be attributed to fuel used for domestic heating. The annual average concentrations are of use in evaluating long-range exposures. All cities in the first table (except St. Louis, which appears in both) have annual averages of 0.015 $\mu g/m^3$ or less. This indicates that some of the highly industrialized smaller cities can have high levels of some pollutants. A review of all available cadmium data uncovered the fact that El Paso, Tex., had the highest 24-hour average recorded, 0.73 $\mu g/m^3$ in 1964; the highest quarterly average, 0.150 $\mu g/m^3$ in 1969; the highest annual average, 0.120 $\mu g/m^3$ in 1964; and the highest percentage of cadmium in the particulate sample, 0.07 percent in 1969. These high values are probably attributable to emissions from a large lead smelter located in the area. In contrast, cadmium levels in 1969 at the 29 active nonurban stations were below the minimum detectable concentration (0.003 $\mu g/m^3$).

Table 5.10. QUARTERLY AND ANNUAL AVERAGE CADMIUM CONCENTRATIONS AT NASN SITES WITH ANNUAL AVERAGE CONCENTRATIONS GREATER THAN 0.015 $\mu g/m^3$, 1969[a]

City	Quarterly average, $\mu g/m^3$				Annual average, $\mu g/m^3$	Cadmium in particulate matter, %
	1	2	3	4		
Denver, CO	0.022	0.015	0.018	0.019	0.018	1.3
Waterbury, CT	0.008	0.029	0.020	0.023	0.020	2.4
E. St. Louis, IL	0.045	0.013	0.016	0.015	0.022	1.8
E. Chicago, IN	0.017	0.046	0.027	0.024	0.028	1.5
Ashland, KY	0.022	0.017	0.026	0.026	0.023	1.3
St. Louis, MO	0.013	0.060	0.041	0.031	0.036	1.7
Helena, MT	0.077	0.004	0.005	0.026	0.028	4.8
Elizabeth, NJ	0.009	0.029	0.018	0.013	0.017	2.3
Newark, NJ	0.015	0.014	0.024	0.099	0.038	5.1
Perth Amboy, NJ	0.024	0.020	0.017	0.011	0.018	2.3
Cincinnati, OH	0.016	0.017	0.019	0.013	0.016	1.4
Allentown, PA	0.011	0.023	0.028	0.017	0.020	1.9
Bethlehem, PA	0.022	0.029	0.015	0.027	0.023	2.6
El Paso, TX	0.083	0.150	0.057	0.130	0.105	7.0

[a]NASN sites listed alphabetically by state.

Table 5.11 presents a summary of cadmium data from both urban and nonurban NASN stations collected after 1965 when the low-temperature sample ashing procedure that prevents loss of cadmium by volatilization was adopted. For each of the years (1966 through 1969), the annual cadmium averages from all the sites are categorized into four concentration intervals. The table illustrates that even though the number of sites has increased over the time period, the cumulative percentage (percentage of sites in that interval or below) within an interval by year has remained essentially the same. The table, however, does not indicate the number of stations (estimated to be at least 50 percent) with cadmium below the minimum detectable concentration. No strong evidence indicates a long-term trend in the cadmium data.

Table 5.11. NUMBER OF STATIONS WITHIN SELECTED CADMIUM CONCENTRATION INTERVALS, 1966 THROUGH 1969[a]

Number and percent of sites	Concentration interval, $\mu g/m^3$				
	<0.010	0.011-0.020	0.021-0.030	>0.030	Total
1969					
Number	169	31	5	3	208
Percent	81	15	2.5	1.5	100
1968					
Number	175	2	2	0	179
Percent	98	1	1	0	100
1967					
Number	119	7	2	5	133
Percent	90	6	1.5	2.5	100
1966					
Number	116	7	3	1	127
Percent	91	5.5	2.5	1	100

5.2.1.1.2 *Chicago and northwest Indiana study*—During the period May through August 1968, Winchester and Harrison[9] conducted a special study of the areawide distribution of heavy metals in Chicago and northwest Indiana. Six sets of 24-hour suspended particulate samples collected at 22 sites in Chicago and at 15 industrial and 11 other sites in northwest Indiana were analyzed for lead, copper, and cadmium. Figure 5.2 shows the concentration for each Chicago site on May 21 and for Indiana sites on May 22, and the corresponding isopleths. Although this represents only one day, it may provide a clue to the distribution of trace metals in the air over a densely populated, highly industrialized area and the influence of concentrated sources on pollutant levels over a large urban area.

5.2.1.1.3 *Miscellaneous studies*—Many special studies have been directed at the definition of the atmospheric burden of cadmium.[10-12] Some were designed to detect the influence of specific sources on the cadmium levels in the immediate area. The results (Table 5.12) clearly show the contributions of cadmium-emitting industries in East Helena, Mont., Sweden, and Japan.

5.2.1.2 *Size Distribution of Particulate Cadmium*[13,14]—Knowledge of the particle size distribution of cadmium-containing suspended particulate matter is essential to an evaluation of the human intake by the respiratory route. Research on the subject has been limited primarily because of the problems associated with analysis for the very minute amount of cadmium present in each particle size fraction collected by available equipment. A summary of results obtained by Lee and coworkers in Cincinnati and St. Louis is presented in Table 5.13.

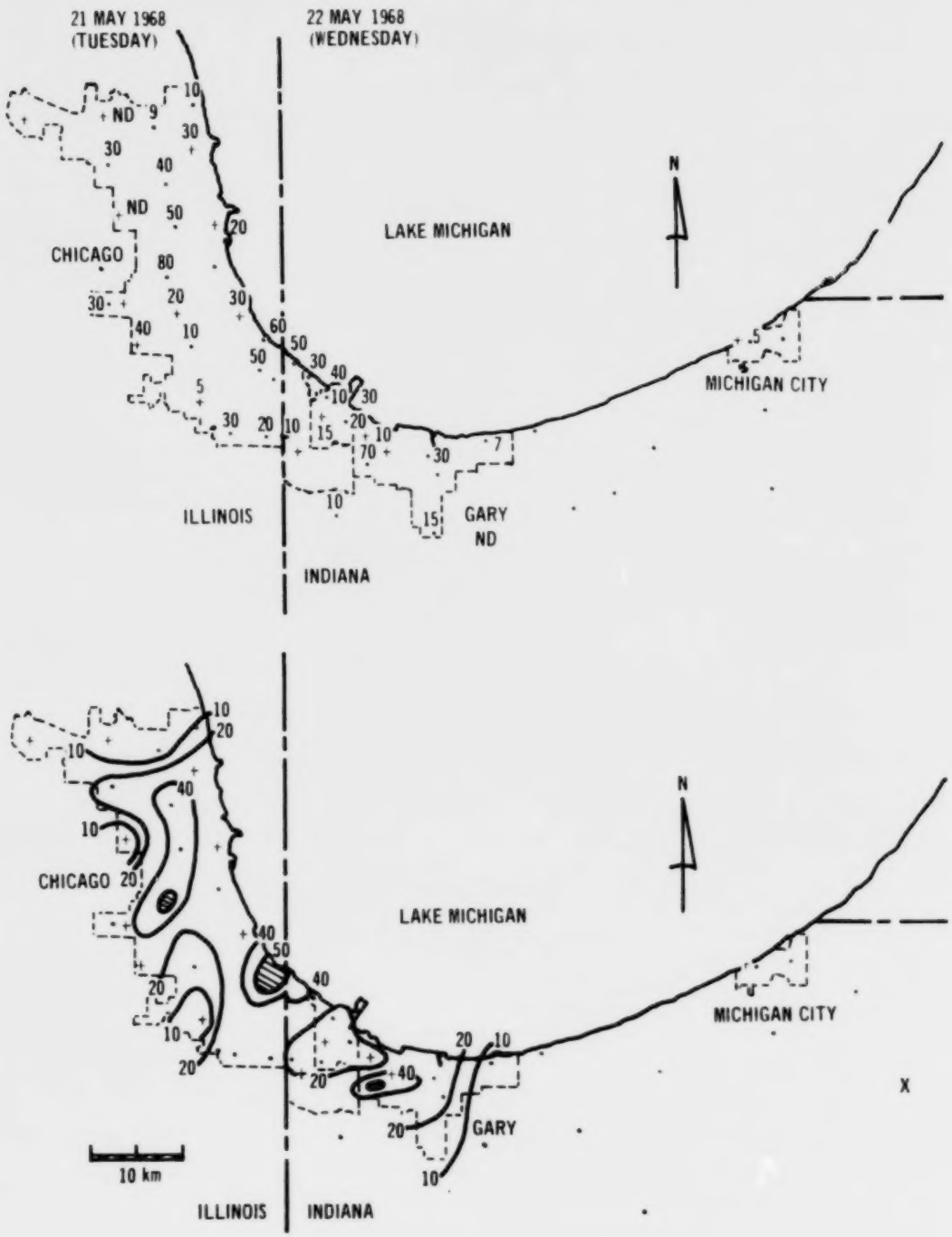

Figure 5.2. Cadmium concentrations (ng/m^3) and isopleths for May 21-22, 1968.[9]

Table 5.12. CADMIUM CONCENTRATIONS IN AMBIENT AIR FOR SELECTED LOCATIONS AND AVERAGING TIMES

Location	Site	Concentration, $\mu g/m^3$	Averaging time	Source distance, meters
Tuxedo, NY[10]	Rural	0.003	Annual	
Sweden[11]	Rural	0.0009	Month	
Stockholm, Sweden[11]	Center City	0.005	Week	
Manhattan, NY[10]	Urban	0.023	Annual	
Bronx, NY[10]	Urban	0.014	Annual	
Helena, MT[12]	Urban	0.03	"Several weeks" 24-hr (max)	7,000
East Helena, MT[12]	Industrial (Pb smelter)	0.06-0.29 0.7	"Several weeks" 24-hr (max)	800-1,300 800
Sweden[11]	Industrial (Cd alloy)	0.6 0.3 5.4	Month Week 24-hr (max)	100 500
Japan, City 1[11]	Near zinc smelter	0.5	Week (of 8-hr values)	100
		0.2	Week (of 8-hr values)	400
Japan,City 2[11]	Near zinc smelter	0.16-0.32	Week (of 8-hr values)	500

The limited available data indicate that a substantial portion of urban particulate cadmium occurs in the respirable size range (< 3.5 μm aerodynamic diameter).

5.2.1.3 *Cadmium in Settled Particulate (Dustfall)*—Most of the particles emitted into the atmosphere eventually settle out and are deposited on soil, water, roadways, building roofs, and other surfaces. The fallout rate is dependent on particle size, density, and wind conditions. Thus, when particles containing cadmium settle out of the air, they contribute either directly or indirectly to the cadmium content of soil and surface waters. Consequently, data on deposition of cadmium should be of value in any study relating to the environmental aspects of that element.

5.2.1.3.1 *Helena Valley, Montana, Area Environmental Pollution Study*[12]—A study was conducted in the Helena Valley during the summer and fall of 1968 to define the extent of pollution in a valley with a large lead smelter and a zinc recovery plant. As part of the study, settled particulate samples were collected monthly at six sites and subsequently analyzed for cadmium. The results, summarized in Table 5.14 and illustrated in Figure 5.3, show that sites 3 and 6, situated nearest the smelter stack, had consistently higher cadmium fallout.

Table 5.13. PARTICLE SIZE DISTRIBUTION OF CADMIUM IN AIRBORNE PARTICULATE MATTER[13,14]

	Cincinnati		St. Louis
	Business 1966	Suburban 1967	Business 1970
Ambient concentration, $\mu g/m^3$	0.08	0.02	0.01
MMD[a], μm	3.1	10	1.5
Percent $<3.5\ \mu m$	45	45	–
Percent $<2\ \mu m$	40	40	65
Percent $<1\ \mu m$	25	20	28

[a]MMD–Mass median diameter (the median diameter of suspended particles aerodynamically determined with reference to spheres of unit density). Fifty percent of the mass is represented by particles with diameters > MMD, and 50 percent of the mass is composed of particles < MMD.

Table 5.14. CADMIUM IN SETTLEABLE PARTICULATES IN THE HELENA VALLEY[12]
(mg/m^2-mo)

	Station and location[a]				
Month	1[b] 1.3 km; 34°	2 4.0 km; 105°	3 0.6 km; 112°	4 7.2 km; 274°	6[b] 0.8 km; 2°
June	0.0	0.0	2.0	0.1	..
July	0.5	0.1	3.0	0.1	..
August	0.2	0.1	1.6	0.1	..
September	0.5	0.3	1.2	0.2	2.2
October	0.5	0.4	1.5	0.2	3.2

[a]Distance and direction from lead smelter stack immediately south of East Helena; degrees are computed from north side of stack in clockwise direction.

[b]Sites 1 and 6 located in East Helena (Figure 5.3).

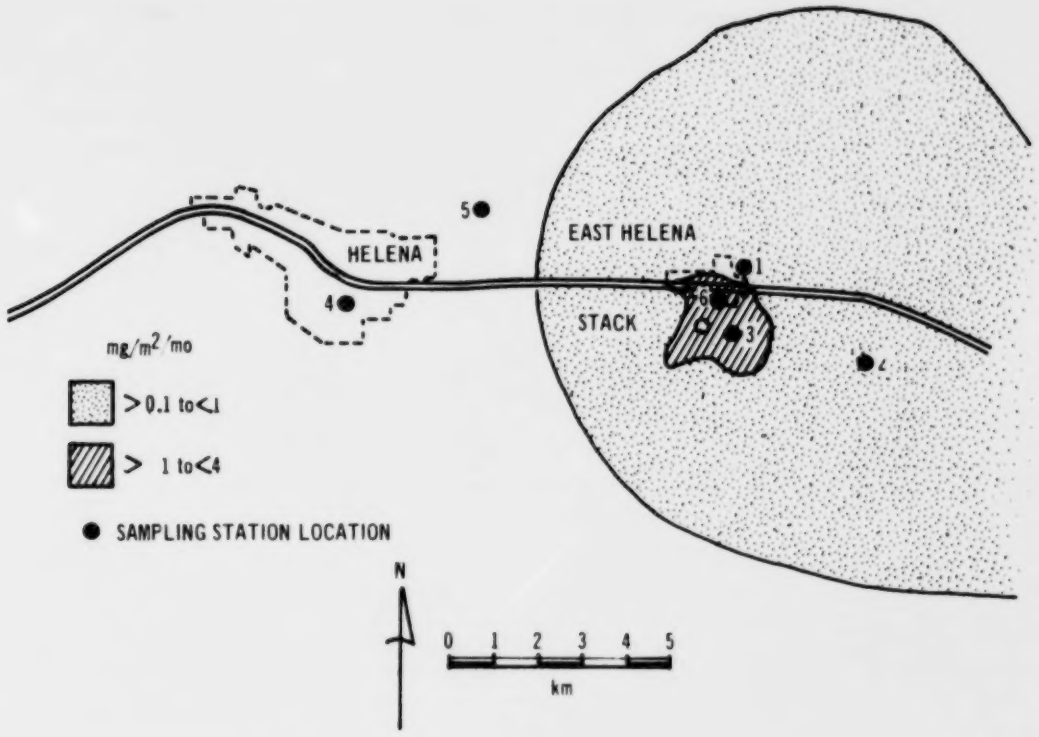

Figure 5.3. Helena Valley Environmental Pollution Study: settleable particulate cadmium distribution.[12]

In the final report of the study, it was concluded that 1 to 4 mg Cd/m^2-mo was deposited within a 1.6-km radius of the smelter and 0.1 to 1 mg/m^2-mo over an area of 150 km^2. No data relative to wind direction during the study are included in the report. For a 5-year period (1949 to 1954) the prevailing wind was from the west (W-18 percent, WNW-14 percent, WSW-13 percent). Consequently, it is not possible to explain the data on the basis of meteorological conditions prevailing during the study.

5.2.1.3.2. *Roadside study*—Creason and coworkers,[15] in an attempt to determine if motor vehicles are sources of trace metal pollutants, determined the cadmium, lead, and zinc content of settled particulate samples collected monthly at four sites in Cincinnati, Ohio, in July, August, and September 1968 (Table 5.15). Samples were collected at distances of 7.6 and 30.5 meters (m) (25 and 100 feet) from the roadway at each site.

In this study, the cadmium fallout did not prove to be substantial, and the amount deposited at 30.5 m was only slightly less than that at 7.6 m, a distribution which could possibly indicate fairly uniform and small particle size and wind turbulence. Although it has been established that some cadmium is injected into the air as a result of wear of automobile tires, which contain small amounts of this element, the data obtained in this study were not suitable for use as a measure of the contribution from this source.

Table 5.15. CADMIUM IN SETTLED PARTICULATES – ROADSIDE STUDY[15]
(mg/m^2-mo)

Site	Distance from road, meters	Month		
		July	August	September
Industrial	7.6	0.084	0.054	0.076
	30.5	0.073	0.046	0.118
Residential	7.6	0.080	0.023	0.077
	30.5	0.067	0.023	0.077
Suburban	7.6		0.061	0.061
	30.5	0.085	0.046	0.046
Suburban / commercial	7.6	0.067	0.252	0.069
	30.5	0.061	--	0.026

5.2.1.3.3 *The 77-city study* – Hunt and coworkers,[16] in September through December 1968, conducted a study of the trace-metal content of settled particulates collected at residential, commercial, and industrial sites in each of 77 midwestern cities. Standard Metropolitan Statistical Areas with more than 1 million or less than 100 thousand people were excluded. The investigators reported geometric mean cadmium deposition (mg/m^2-mo) for all cities as a group: residential 0.040, commercial 0.063, and industrial 0.075. The purpose of this study was to examine a possible relationship between cadmium, lead, and zinc pollution and cardiovascular disease; however, careful analysis of the cadmium fallout data failed to uncover any significant relationship.

5.2.1.3.4 *Swedish study*–Olofson, cited in Friberg et al.[11] measured deposition of cadmium emitted from a Swedish factory (Finspong Plant) at the rate of 460 kg/month. Samples were collected at different times at seven sites located around the plant during one or more years in the period 1968 to 1970.

The results of this study (Table 5.16) dramatically illustrate the impact of a single major source on the quality of the surrounding environment. The cadmium fallout from this source contributed substantially to the pollutant burden of the surrounding area.

5.2.2 Water

The soluble cadmium content of natural waters is low. The major portion will be found in suspended particles and in the bottom sediments. In water considered not to be polluted by cadmium, concentrations of less than 1 μg/liter (ppb) have been reported. In samples from a site 500 meters downstream from a cadmium-emitting factory, the cadmium content of the water was found to be 4 ppm, while the bottom sediments contained 80 ppm (dry weight).[11]

The proposed U. S. interim drinking water standard (1975) for cadmium is 10 μg/liter (0.01 ppm). The average cadmium concentration in main streams and lakes draining 16 major U. S. watersheds was 9.5 μg/liter as measured from 1962 to 1967.[17]

A number of studies have shown that the cadmium concentration of municipal water systems varies from the inlet valves to the outlet taps with the latter being the higher. The increase has been attributed to the cadmium content in the pipes. The cadmium content in galvanized iron pipe has been reported as 360 ppm;

polyvinyl chloride (PVC) pipe contains from 0.2 to 2.0 ppm cadmium. The variation in the cadmium content of the water is apparently dependent upon the pH and temperature of the water and the residence time in the pipe. Increases in the pH and/or carbonate concentration resulted in lower levels of cadmium. Results of a study by Schroeder[18] are shown in Table 5.17.

Table 5.16. DEPOSITION OF CADMIUM AROUND AN EMITTING FACTORY, 1968 TO 1970[11]

	Distance from factory, km						
	0.1	0.3	0.3	0.5	0.7	1.0	10.4
Direction	S	NE	N	NNW	NE	SW	ENE
Number of years	3	1	1	2	3	2	1
Number of measurements	10	2	5	8	10	6	5
Deposition, mg/m^2-mo							
Minimum	4.0	0.7	1.2	0.5	0.4	1.0	<0.03
Maximum	40.0	1.8	5.3	3.0	4.0	3.5	0.7
Average	16.7	1.3	3.4	1.7	1.3	1.8	0.3

In 2,595 community water samples analyzed by the Bureau of Water Hygiene in 1969,[19] the cadmium content was found to exceed the mandatory limit in 0.2 percent of the samples.

A study by the U. S. Geological Survey (cited by Fulkerson[2]), in which 720 water samples were collected from lakes and rivers throughout the United States and analyzed for the presence of various elements, showed cadmium present in 42 percent of the samples. The range was from 0.001 to 0.01 mg/liter. The general conclusion was that higher concentrations of cadmium in water are usually found in areas of high population density.

Table 5.17. ZINC AND CADMIUM IN MUNICIPAL WATER, BRATTLEBORO, VT[18]
(ppb)

	Zinc	Cadmium
Inlet	3.5	2.1
Spillway	3.5	2.5
Town water main		14.0 to 21.0
Cold running tap water	160	8.3
Stagnant - in pipes	1830	15.0 to 77.0
Hot running tap water		21

5.2.3 Soil

The amount of cadmium in soils, unless contaminated by human activities, is highly dependent upon the underlying parent rock. Organic matter usually has a higher cadmium content than other soils.[2] In soils not known to be polluted by cadmium, concentrations of less than 1 ppm were reported.[11] Bowen[20] lists the cadmium concentration of soil as being 0.06 ppm.

Analysis of the soil at the Virgin Islands Agricultural Station[18] revealed 3.38 ppm cadmium in soil fertilized with phosphatic fertilizer but only 0.15 ppm in untilled and 0.8 ppm in tilled, unfertilized soil.

In the Helena, Montana, study,[12] soil concentrations decreased with distance from the smelter complex:

68 ppm at 1.6 km (1 mile)
17 ppm at 3.2 km (2 miles)
4 ppm at 6.4 km (4 miles)

Similar results have been found in Japan in the vicinity of emission sources.

Phosphate fertilizers contain cadmium. Because of the wide usage of phosphate fertilizers, cadmium could be added to soil in this manner; however, because phosphates tend to precipitate cadmium, it would not be available to plant or animal life unless converted to a soluble form.[2]

Cadmium can be added to the soil in sewage sludge. Studies in Sweden and England have reported the addition of metals to soil in this form. In Sweden, the median concentration of cadmium in sludge was 12 ppm dry weight; the range was from 2 to 61 ppm.[21]

Deposition of atmospheric particulates in the vicinity of emission sources, water runoff from polluted sources (factories and mines), use of polluted water in irrigation, and fertilization with cadmium-containing sewage sludge may all add to the cadmium content of soil.

5.2.4 Food

The cadmium concentrations in food, despite many studies and analyses, are still subject to debate. The mechanisms involved in the transport of cadmium from its primary sources into the physical environment and then through the various pathways into the food chain are still not clear. In addition, the results of the various studies are influenced by the following factors:

- Varying ability of different species of plants and animals to concentrate cadmium.
- Accuracy of the data produced by the analytical methods used.
- Possibility of sample contamination.
- Interpretation of the data.
- Regional differences in soils in which the food plants are grown and water sources when plants are irrigated.
- Processing through which the food has passed.[2,11]

Friberg et al.[21] indicate that foodstuffs generally contain less than 0.05 ppm cadmium (wet weight). Marine organisms, such as shellfish, and the liver and kidney of calves or swine, however, may contain much higher quantities of cadmium, even in unpolluted areas. Rice and wheat also tend to accumulate cadmium to concentrations of more than 1 ppm in polluted areas (see Table 5.18).

Table 5.18. UPTAKE OF CADMIUM BY RICE AND WHEAT[2]

Addition of Cd to soil, % CdO	Rice Cd, ppm			Whole grain wheat		Factors of increase in plant concentration for each 10-fold increase in soil		
						Rice		
	Yield, %	Polished (10%)	Bran	Yield, %	Cd, ppm	Polished	Bran	Whole grain wheat
0	100	0.16	0.59	100	0.44			
0.001	100	0.28	0.79	106	8.27			
0.003	92	0.40	0.84	72	15.5	2.8	2.0	3.6
0.01	92	0.78	1.60	16	29.9			
0.03	93	1.37	2.68	13	41.4	2.1	1.8	2.0
0.1	69	1.62	2.94	3	60.7			
0.3	32	1.94	3.19	3	48.6	...	...	2.3
0.6	19	1.37	3.94	2	90.8			
1.0	1	4.98[a]		1	139.0			

[a]Unpolished.

Cadmium levels in food samples collected from 1968 to 1970 from 30 markets in 24 different cities in the United States are shown in Table 5.19. Table 5.20 shows the cadmium content of selected foods from several different countries.

Table 5.19. CADMIUM CONTENT IN DIFFERENT FOOD CATEGORIES IN U.S.[21]

Type of food[a]	Cadmium, ppm wet weight[b]			
	1968-1969		1969-1970	
	No. ≥0.01	Maximum	No. ≥0.01	Maximum
Dairy products	10	0.09	9	0.01
Meat, fish, and poultry	21	0.06	22	0.03
Grain and cereal products	27	0.08	27	0.06
Leafy vegetables	27	0.08	28	0.14
Legume vegetables	16	0.03	10	0.04
Root vegetables	24	0.08	27	0.08
Garden fruits	25	0.07	27	0.07
Fruits	15	0.38	10	0.07
Oils, fats, and shortening	27	0.13	28	0.04
Sugar and adjuncts	18	0.07	27	0.04
Beverages	8	0.04	9	0.04
Potatoes	--	--	29	0.08

[a]Total number of samples: 30.

[b]Analyzed by atomic absorption and/or polarography at sensitivity of 0.01 ppm.

Table 5.20. CADMIUM IN SELECTED FOODS IN VARIOUS COUNTRIES[11]
(ppm wet weight)

Country	Potato	Tomato	Wheat flour	Milk
U.S.A.	0.001	0	0.07	0.0015-0.004
Western Germany	0.039	0.015	0.047	0.009
Czechoslovakia	0.09		0.02	0.01
Rumania	0.017	0.013		
Japan (non-polluted areas)	0.038	0.032	0.025	0.003

In the comparison of concentration data from different countries, consideration should be given to the location of the agricultural area in relation to the cadmium emission sources and the contamination processes. The majority of the food consumed in the United States is grown in areas remote from primary emission sources. Similar conditions do not exist in Japan.

Cadmium concentrations in U. S. oysters have been reported to range from 0.1 to 7.8 μg/g wet weight on the east coast and 0.2 to 2.1 μg/g on the west coast.[22]

In general, it may be concluded that most foods, not from cadmium polluted areas, contain less than 0.05 μg/g of cadmium, wet weight.

5.2.5 Tobacco

Analyses of cigars, cigarettes, pipe tobacco, and snuff reveal that tobacco in these forms contains appreciable amounts of cadmium and nickel. When tobacco is smoked, cadmium is released into the mainstream and may be inhaled. Menden et al.[23] found that American cigarettes have amounts ranging from 1.56 to 1.96 μg per cigarette. Through the use of a smoking machine, which puffed 35-ml puffs for 2 seconds every minute, the investigators found that the particulate phase of the mainstream contained 0.10 to 0.12 μg per cigarette. A person who smokes a pack of cigarettes (20 cigarettes) a day inhales about 2 μg of cadmium per day (see Table 5.21, and 5.22). The data presented in Table 5.22 suggest that 38 to 50 percent of the cadmium in smoked cigarettes is present in the sidestream. Cadmium, therefore, not only is inhaled by the smoker but enters the air in the smoke from the sidestream (smoke from cigarette not drawn in by smoker) and may be inhaled from there also.

Table 5.21. METAL CONTENT OF TOBACCO PRODUCTS[23]

	Metal content,[a] μg/cigarette		
	Cadmium	Nickel	Zinc
Kentucky reference[b] cigarettes (KR)	1.56± 0.19 (6)[c]	4.25± 0.18 (2)	33.4± 2.4 (7)
Commercial brand[b] cigarettes (CB)			
Batch 1	1.90± 0.14 (4)	--	38.9± 9.0 (4)
Batch 2	1.96± 0.11 (4)	7.55± 0.15 (4)	20.0± 0.8 (4)

[a]Values are mean ± standard deviation.

[b]KR cigarettes weighed 1.12 ± 0.04 grams and CB cigarettes weighed 1.12 ± 0.10 grams.

[c]Value in parentheses denotes number of samples.

Table 5.22. TRACE-METAL CONTENT OF CIGARETTE FRACTIONS[23]

Fraction	Metal content[a,b]		
	Cadmium	Nickel	Zinc
KR[c] cigarettes			
Smoked portion (73% of total)	1.14	3.10	24.3
Smoked butt	0.56 ± 0.03(6)	1.33 ± 0.07 (2)	12.4 ± 1.9 (6)
TSC[c] (mainstream particulate phase)	0.12 ± 0.03 (5) 10.1%	0.08 2.6%	0.36 1.5%
Ash	0.45 ± 0.03 (4) 39.4%	1.81 ± 0.16 (2) 58.4%	21.3 ± 4.7 (5) 87.6%
Sidestream[d]	0.43 38%	1.03 33%	-0.66 3%
CB[c] cigarettes			
Smoked portion (73%)	1.43	5.51	14.6
Smoked butt	0.67 ± 0.02 (4)	2.64 ± 0.17 (4)	7.6 ± 0.8 (4)
TSC[c] (mainstream particulate phase)	0.10 ± 0.01 (2) 7%	0.02 ± 0.01 (2) 0.4%	0.06 ± 0.01 (2) 0.4%
Ash	0.48 ± 0.02 (4) 33.5%	4.27 ± 0.20 (4) 77.5%	11.9 ± 0.5 (4) 81.5%
Sidestream[d]	0.72 50%	0.62 11%	0.40 3%

[a]Concentrations are in μg per fraction listed. Values are means ± standard deviation or calculated values. Parentheses indicate the number of samples.

[b]Percentages were calculated on basis of smoked portion.

[c]KR = Kentucky reference; TSC = tobacco smoke condensate; CB = commercial brand.

[d]Sidestream was calculated by subtracting the values of smoked butt, TSC, and ash from the total cigarette value given in Table 5.22. (Enrichment can be estimated by subtracting the calculated value for unsmoked butt from the experimental value given.)

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6. ENVIRONMENTAL EXPOSURE

6.1 HUMAN EXPOSURE AND INTAKE RATES

Cadmium enters the body mainly through ingestion or inhalation. Skin penetration by soluble cadmium compounds can take place, but this exposure route is of minor importance to the general population. The estimated cadmium concentrations and the media through which human exposure may occur are listed in Figure 6.1.

6.1.1 Food

Whereas the estimates of exposure via air or water are relatively accurate, reliable estimates of exposure via food are difficult to obtain. There are several reasons for this lack of data. One is the difficulty of analyzing cadmium in food; another, the fact that, whereas cadmium often is determined in the raw food material, the actual exposure takes place through mixed diets, which have been processed in different ways. This processing may result either in the loss of cadmium during cooking or result in further contamination from the utensils used.

Because of ambient cadmium concentrations, consumption of foods, even from uncontaminated areas, will result in a daily intake of approximately 50 μg. Estimates of daily intakes in selected countries are given in Table 6.1. These estimates are based on cadmium concentrations in raw agricultural products and available data on consumption of different foodstuffs.

Table 6.1. DAILY INTAKE OF CADMIUM VIA FOOD IN DIFFERENT COUNTRIES[2]

Country	Cadmium, μg/day	Measurement method
United States	4 to 60	Dithizone
West Germany	48	Atomic absorption after extraction
Rumania	38 to 64	Dithizone
Czechoslovakia	60	Dithizone or isotope dilution or atomic absorption
Japan (nonpolluted area)	59	Dithizone or atomic absorption after extraction

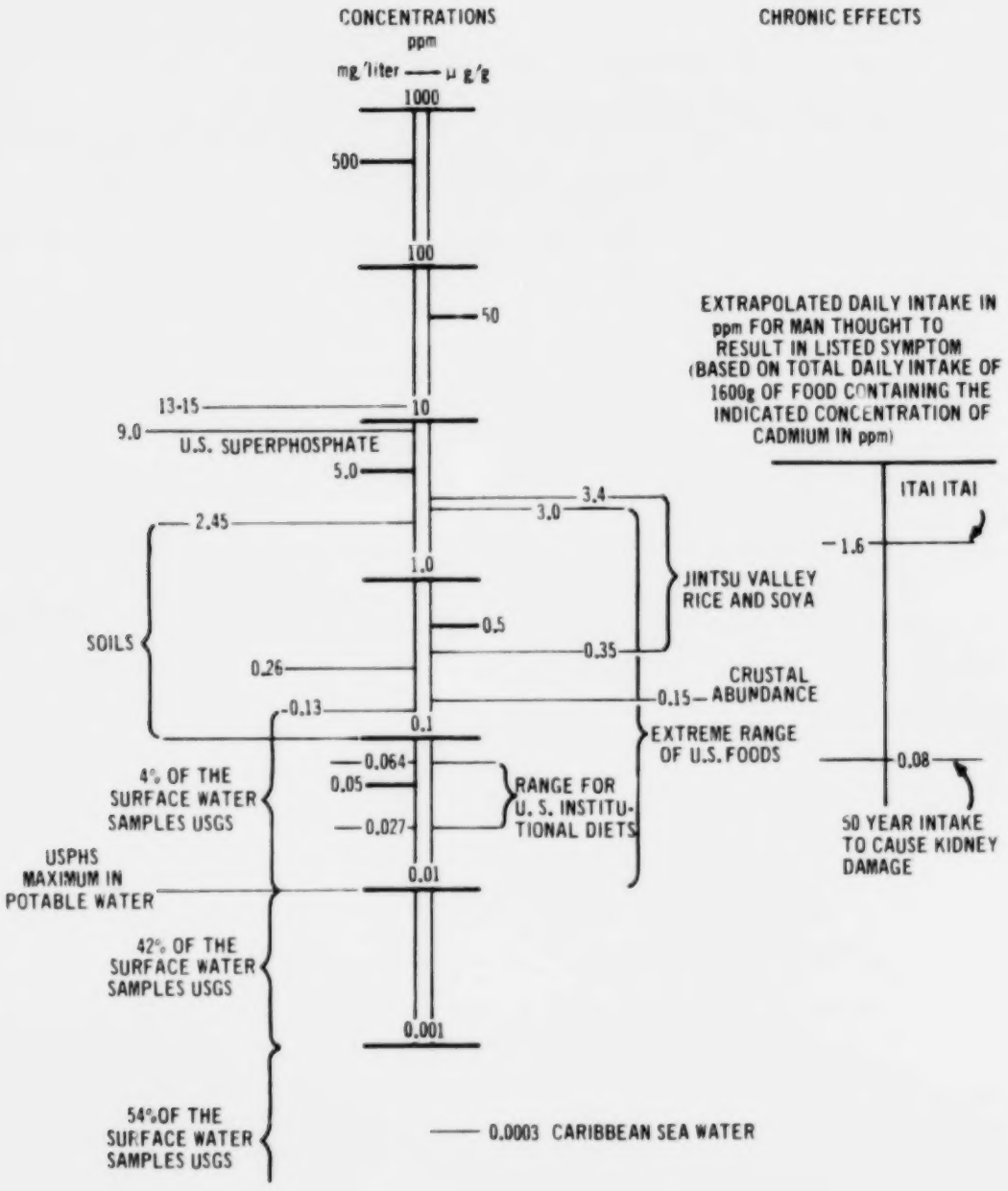

Figure 6.1. Cadmium concentrations of surface waters, soils, and foods and estimated dose levels resulting in various symptoms and effects in humans.[1]

As can be seen, there if fairly good agreement between estimates obtained in different countries. It should be pointed out, however, that because of the method used, U.S. values are higher. The method using extraction of the element is more accurate.

Generally, there is agreement that fruit has the lowest cadmium levels and that shellfish and the kidney and liver of animals have the highest concentrations.

Polluted areas present a different picture. Rice in the Jintsu Valley of Japan was found to have a cadmium content 30 times greater than in nonpolluted areas.[3] The rice fields were polluted by industrial activities.

A study by EPA in East Helena, Mont. indicates that up to 83 μg/day of cadmium could be added to an ordinary diet by the consumption of fruits and vegetables grown in soil contaminated by cadmium.[4]

Eating shellfish can also add to the amount of cadmium ingested. The Eastern oyster was found to contain an average of 3.1 ppm; the soft shell clam and Northern Quahaug clam contained 0.27 and 0.19 ppm, respectively.[5] Seawater has an average cadmium concentration of 0.0001 ppm, and the biological accumulation of cadmium by shellfish ranges from 100 to more than 3,000 ppm.

6.1.2 Air

In ambient air, mean yearly cadmium concentrations may range from less than 0.001 to 0.05 $\mu g/m^3$. Higher values have been reported in areas near cadmium-emitting industries, such as in Sweden where monthly means of up to 0.3 $\mu g/m^3$ have been measured.[2]

Few data dealing with the deposition, retention, and elimination of cadmium aerosol exist.[2] If the assumption is made, however, that the deposition of inhaled cadmium aerosols in the respiratory system is similar to the behavior of other particulate matter, then the deposition depends not only on the air concentration but also on particle size. It can be said, then, that the amount of cadmium inhaled depends on the volume of air (average inhalation is 20 m^3/day) and the ambient concentration of cadmium. The fraction of the inhaled portion that is deposited in the lung depends on the particle size—the smaller the particle, the greater the rate of deposition.

6.1.3 Smoking

Cadmium has been found in cigarettes in amounts of about 1 to 2 μg per cigarette.[6-8] Using smoking machines and standardized methods, it has been shown that 0.1 to 0.2 μg of cadmium per cigarette will be found in the mainstream.

The smoking of 20 cigarettes per day, then, could cause the inhalation of 2 to 4 μg of cadmium depending on the amount of smoke inhaled. Autopsies made of smokers and nonsmokers substantiate this statement.[9] It was found that there was a significant correlation between the number of years of cigarette smoking and the amount of cadmium in kidney, liver, and lungs.

The smoker is not the only person exposed to cadmium, however. Studies indicate that more cadmium is emitted from cigarettes in the sidestream than from the mainstream. Sidestream smoke has been shown to contain from 0.43 to 0.72 μg of cadmium per cigarette.[8]

6.1.4 Water

The cadmium concentration of waters, in areas unpolluted by cadmium, has been reported as being 1 μg/liter (1 ppb) or less.[2] The proposed EPA drinking water standard is 10 μg/liter (0.01 ppm). Although higher concentrations for drinking water have been reported in certain areas of the United States, drinking water generally contains less than 1 μg/liter. At this level, consumption of up to 4 liters of water per day

would result in the ingestion of only a few micrograms. At a concentration of 10 μg, a daily intake of 20 to 40 μg of cadmium would result if 2 to 4 liters of water were consumed.

6.1.5 Soil

Comprehensive studies of cadmium exposure from soils have not been made. Cadmium in the soil may be taken up by plants and thus become available to man through food.

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7. MECHANISMS OF EXPOSURE AND RESPONSE

7.1 RESPIRATORY ABSORPTION

Respiratory absorption is one of the chief avenues of entrance of pollutants into the human body. There are, however, very few data dealing with the deposition, retention, and elimination of cadmium aerosols entering the lungs.[1] The rate of deposition of particles in the lungs is dependent on particle size as well as the concentration in the air.[1]

Cadmium is absorbed to a large extent after inhalation. Absorption occurs primarily in the lungs, but occurs also in the gastrointestinal tract after mucociliary clearance. Data dealing with human absorption are not available, but animal experiments suggest an absorption of between 10 to 40 percent of the cadmium inhaled.[2] For instance, calculations based on experiments by Friberg[3] in which rabbits were exposed to cadmium iron oxide dust for several months showed that about 30 percent of the inhaled cadmium was absorbed into the body.

7.2 GASTROINTESTINAL ABSORPTION

The absorption and excretion of radioactive cadmium in five human volunteers was studied by Rahola et al.[4] They found that during the 3 to 5 days following the administration of labeled cadmium (^{115}Cd) in calf-kidney suspension, about 70 percent of the activity was eliminated. The total ingestion of cadmium was about 100 μg. Most of the excreted activity was in the feces. Rapid elimination of the tracer continued until about 6 percent of the dose remained in the body, indicating an average absorption of at least 6 percent.

Experiments in adult animals have shown that between 1 and 3 percent of the oral dose of cadmium is retained in the body several days after exposure. These results suggest that a considerable amount of unabsorbed cadmium will be excreted in feces as late as between the 5th and 10th day.[2] The decrease in whole-body retention of radioactive cadmium was very slow from 20 days to 2 months after exposure.[2]

The influence of calcium deficiency on absorption and retention of cadmium after oral intake has been studied. The studies indicated that rats on low-calcium diets accumulate more cadmium in their livers and kidneys than rats on high-calcium diets.[1,2] Vitamin D and the protein level of the diet appear to affect cadmium retention in animals since (1) rachitic chickens absorb more cadmium when vitamin D is administered along with cadmium[1] and (2) mice on a low-protein diet for 24 hours preceding and following an oral dose of cadmium chloride absorbed about twice as much cadmium as mice on a high-protein diet for the same period.[1]

The available data, therefore, indicate that the absorption rate of cadmium is about 6 percent in male adult human beings. Absorption may be higher for individuals with a calcium deficiency or a greater calcium demand.[2]

7.3 TRANSPORT AND DISTRIBUTION

Most of the work on the transport and distribution aspects of cadmium metabolism has been done in animals. Because such a small proportion of orally administered cadmium is absorbed, it has not been

possible to study the distribution of radioactive cadmium in the blood after ingestion of the materials. After interperitoneal administration, most of the cadmium initially found in the blood is associated with the plasma. It is then rapidly cleared from the plasma and, after about 12 to 24 hours, the concentrations in the whole blood begins to rise again. This is caused by an increase in the cadmium content of the red blood cells, which, at that time, also contain metallothionein.[1] When animals are given repeated injections of cadmium, the concentrations of the metal in the erythrocytes becomes many times greater than the concentration in the plasma. Further distribution of cadmium throughout the body is dependent on the elapsed time since the absorption of the material. The largest concentrations of the metal are found in the liver and the kidneys. The concentrations of the metal in these organs are roughly proportional to the intake of cadmium; but as the dose of cadmium is increased, the proportion in the liver becomes greater.[1]

In individuals without known "over" exposure to cadmium, the mean level in whole blood is less than 1 μg/100 ml. In workers exposed to cadmium, concentrations of up to 30 μg/100 ml of whole blood have been found. In workers exposed to cadmium, the blood cadmium concentration will decrease when exposure stops.[1]

Cadmium concentrations have been determined in the organs of various populations. In the United States, the average concentration of cadmium in the liver of "normal" individuals varies with age. The values usually do not exceed 2 μg/g of tissue (wet weight). "Normal" values from two Japanese studies are higher.[1]

The placenta is an effective barrier for cadmium, and the concentration in the liver of the newborn is less than 0.002 μg/g.

Data on the concentration of cadmium in the livers of workers who have been exposed to cadmium oxide dust in the past have shown that there is no tendency for the concentration to decrease substantially with time following the cessation of exposure to cadmium.[1] Data from the United States, Japan, Sweden, and East Germany show that there is a progressive increase in the concentration of cadmium in the renal cortex with increasing age. The average concentration of cadmium in the renal cortex by age groups in the United States is shown in Table 7.1

Table 7.1. AVERAGE CADMIUM CONCENTRATION IN RENAL CORTEX BY AGE GROUPS IN THE UNITED STATES

Age group	Cadmium content, μg/g wet weight
1 to 9	7
10 to 19	25
20 to 29	30
30 to 39	46
40 to 49	53

After age 50 to 60, there is a decline in the concentration of cadmium in the renal cortex. Why this occurs is not known. Recent investigations by Hammer et al.[5] have shown that in North Carolina the average cadmium concentration at age 50 is about 25 μg/g of tissue (wet weight). This result is similar to values reported from Sweden and East Germany, but lower than in areas in Japan regarded as not being polluted by cadmium (Table 7.2).

Table 7.2. MEAN CADMIUM CONCENTRATIONS IN RENAL CORTEX AT AGE 50[1,2]

Country	Sex	Cadmium content, μg/g wet weight
East Germany	M	30
East Germany	F	15
Sweden (Stockholm)	M and F	30
United States (large cities)	M and F	50
United States (North Carolina)	M and F	25
Japan (Kobe)	M and F	60
Japan (Kanazawa)	M and F	85
Japan (Tokyo)	M and F	125

7.4 EXCRETION

7.4.1 Urine

The average normal excretion of cadmium in urine is less than 5 μg/day. Most of the studies done in the past years have found the excretion to be 1 to 2 μg/day in adults. Recent investigations in Japan have shown that the urinary excretion will increase with age, being about 0.5 μg/liter in children and about 2 μg/liter at age 40.[6,7]

Various studies have found cadmium excretion varying from less than 1 μg/day to 100 μg/day. It has recently been shown that in workers with long-term exposure to relatively low concentrations of cadmium oxide dust, urinary excretion of cadmium generally did not exceed 10 μg/g creatinine in workers with normal urine protein electrophoretic patterns, whereas workers with tubular proteinuria excreted considerably larger amounts. Renal tubular dysfunction may thus cause increased excretion of cadmium. In workers with short-term, high-level exposure to cadmium oxide dust or fumes, the urinary excretion of cadmium may sometimes be high without any changes in renal function. In these cases the increased urinary excretion probably reflects the more recent exposure than the body burden.[1]

The increased urinary excretion when there is renal damage explains why renal concentrations of cadmium often have been quite low in autopsied workers with severe morphological kidney changes.[1]

7.4.2 Feces

Animal experiments have shown that a small percent of injected cadmium will be excreted via the alimentary tract. This excretion is mainly dependent on recent exposure.[1] The data do not indicate the role this excretion route plays in human beings.[1]

7.4.3 Hair

A small amount of cadmium is excreted in the hair. Although this excretion is not important as a means of ridding the body of cadmium, it has been explored as a possible indicator of cadmium exposure. The method is complicated by the fact that hair can be contaminated by metals in the atmosphere as well as metals in hair lotions and hair spray.[1]

7.5 BODY BURDEN

Schroeder and Balassa[8] estimated the total body burden of cadmium to be about 30 mg in the "standard American man." In a study in North Carolina, Hammer et al.[5] found the corresponding figure to be about 15 mg, which is similar to what has been found in some European countries.

According to Friberg et al.[1] the total body burden at age 50 in noncontaminated areas in Europe is 15 to 20 mg and in Japan 40 to 80 mg. Recent studies of Tsuchiya et al.[7] support the conclusions that even in so-called nonpolluted areas of Japan, body burdens of cadmium are much higher than in other industrialized areas of the world.

Earlier assumptions that smokers will have higher body burdens than nonsmokers have been verified by the results of Lewis et al.[9] They determined the cadmium content in the kidney, liver, and lungs of 45 male smokers (mean age 60 years) and in 22 male nonsmokers (mean age 60 years). It was possible to calculate the number of "cigarette pack years" for each smoker. Cadmium in kidney, liver, and lungs of nonsmokers averaged 6.6 mg; in smokers, the corresponding figure was 15.8 mg. There was a significant association between the number of pack years and cadmium accumulation.

About half of the total cadmium will be found in liver and kidneys together – about a third in the kidneys alone. In exposed workers, the percentage in the liver increases in relation to the kidney.

7.6 BIOLOGICAL HALF-TIME

The biological half-time of cadmium in humans is extremely long. This conclusion is based on a model for cadmium accumulation in the body based on the concept that one-third of the body burden was in the kidneys.[1] Kjellstrom[10] and Tsuchiya et al.[11] used autopsy data and calorie consumption in these calculations. Biological half-times of from 18 to 33 years were thus obtained. Tsuchiya et al.[12] calculated the biological half-time to be about 17 years in the kidney and 6 years in the liver, based on renal and liver burdens of cadmium obtained by autopsies on inhabitants of Tokyo.

In these reports, it was noted that many parameters must be taken into account when calculating biological half-time, such as changes in food intake and changes in kidney weight with age. Changes in exposure over the years must also be taken into account.[13] All data continue to favor a very long biological half-time, although the question of the exact biological half-time of cadmium in the human body is still under discussion.[2]

7.7 CONCLUSIONS

Current knowledge of the mechanisms of exposure and response lead to the following conclusions:

- Uncertainties with regard to absorption rates after inhalation in humans and other animals still exist and demand extensive investigation.
- Calcium deficiency will cause a considerable increase in cadmium absorption whether exposure occurs through food or drinking water.

- The initial accumulation of cadmium in red blood cells is followed by a decrease and later by a new accumulation. This distribution is associated with a buildup of metallothionein in the cells. After exposure to cadmium ceases, blood levels gradually drop.

- Repeated exposure to small amounts of cadmium results in its continuous buildup in liver, kidneys, and other organs.

- In human beings, an absorption of ingested cadmium of up to 10 percent must be considered possible when conditions such as a calcium or protein deficiency exist.

- Total body burden of cadmium at age 50 is approximately 15 to 20 mg in Europe; 15 to 30 mg in the U.S.; and 40 to 80 mg in Japan.

- In normal human beings, daily excretion of cadmium via urine is very low, 2 μg/liter or less.

- Estimates based on mathematical models show that the half-time for cadmium in the total body may be between 10 and 30 years. Many uncertainties still exist with regard to biological half-time in total body and in different organs. It is obvious, however, that the biological half-time of cadmium is extremely long.

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8. EFFECTS

8.1 HUMAN IMPACT

8.1.1 Respiratory Effects of Cadmium Exposure

8.1.1.1 *Acute Effects*–Animal studies indicate that effects from the inhalation of cadmium oxide or cadmium chloride aerosols occur in three clearly demarcated stages:

- Acute pulmonary edema, developing within 24 hours of exposure.
- Proliferative interstitial pneumonitis, observed from the third to the tenth day after exposure.
- Permanent lung damage in the form of perivascular and peribronchial fibrosis.[1]

The first two stages have been confirmed clinically or through autopsy for humans.[1]

The cadmium dose that resulted in two human deaths was calculated to be approximately 2,500 mg/m^3-min. This represents an exposure to 100 mg/m^3 for 25 minutes or 50 mg/m^3 for 50 minutes.[1]

8.1.1.2 *Chronic Effects*–Friberg[2] found emphysema of the lung among male workers chronically exposed to cadmium oxide dust in an alkaline battery factory in Sweden. Quantitative data concerning the exposure levels were incomplete; however, a range of 3 to 15 mg/m^3 was reported. Several other instances of lung damage, including pulmonary sclerosis, bronchitis, and emphysema have been reported.[1] Little information is available, however, concerning the possible association between respiratory disease and exposure to cadmium via ambient air. The establishment of dose-response relationships is hindered at present because time-weighted average exposures are available only for short time spans.[1]

8.1.2 Systemic Effects of Cadmium Exposure

8.1.2.1 *Kidney Effects*–In fatal cases of acute cadmium poisoning via inhalation, pathological changes have been found in the kidneys.[1] Transient proteinuria has been detected in individuals with nonlethal cadmium exposure.[1]

Prolonged exposure to cadmium oxide dust has given rise to renal damage in factory workers. Proteinuria is the most common clinical manifestation of this type of renal damage.[1] Piscator and Lind[3] have shown that the magnitude of proteinuria is related to the length of exposure. Glycosuria, amino-aciduria, diminished concentrating capacity, and renal stones have also been reported in cadmium-exposed workers. Although proteinuria occurs frequently in cadmium workers, its magnitude tends not to progress once the exposure to the metal ceases.

The relationship between the dose of cadmium and the degree of kidney damage is poorly defined. Present data are inadequate to accurately quantitate the magnitude of the cadmium exposure of industrial workers. Furthermore, because there is no constant relationship between the concentration of cadmium in the blood and the cadmium content of the kidney, the former cannot be used to estimate the dose of cadmium in the kidneys.

On the basis of data from workers exposed to cadmium and from animals manifesting functional and morphological changes in the renal cortex following exposure to cadmium, the authors of *Cadmium in the Environment*[1] have concluded that a cadmium concentration of about 200 ppm (wet weight) in the renal cortex is a "critical concentration." When a level of 200 ppm is reached, the first sign of tubular dysfunction (tubular proteinuria) may appear in sensitive persons. Estimates of the long-term exposure necessary to achieve a concentration of 200 ppm of cadmium in the renal cortex have been made (Table 8.1).

Table 8.1. ESTIMATED MINIMUM CADMIUM LEVELS VIA INHALATION OR INGESTION NECESSARY FOR REACHING 200 ppm (WET WEIGHT) OF CADMIUM IN RENAL CORTEX (TOTAL BODY BURDEN: 120 mg CADMIUM)
($\mu g\ Cd/m^3$)

Exposure, years	Total daily ingestion			Ambient air[a]			Industrial air[a]		
	Retention rate, %			Retention rate, %			Retention rate, %		
	2.5	5	10	10	25	40	10	25	40
10	1324	662	331	16.2	6.5	4.1	52.5	21.0	13.1
25	530	265	132	6.5	2.6	1.6	21.0	8.4	5.2
50	265	132	66	3.2	1.3	0.8	10.5	4.2	2.6

[a]A lung ventilation of 20 m^3 per day has been used for evaluation of ambient air exposure. A lung ventilation of 10 m^3 per 8 hours for 225 days per year has been used for evaluation of industrial air exposure. No corrections have been made for cumulative effects of different types of exposure, including tobacco smoking. A linear approximation of the accumulation of cadmium has been used.

Using Table 8.1, it can be noted that a daily oral intake over 50 years of 100 to 150 μg cadmium with a 5 percent retention may give rise to renal dysfunction. Long-term exposure to low levels of cadmium usually result in about one-third of the cadmium remaining in the kidneys.[1]

Calcium deficiency has been shown to increase the absorption of cadmium.[1] Exposure via water and smoking should also be taken into account.

8.1.2.2 *Liver Effects*—In workers suffering from acute cadmium poisoning as a result of a toxic exposure to cadmium oxide fumes, microscopic changes were evident in the liver. Increases in serum gamma globulin have also been reported in several victims. Whether these changes represent a direct toxic effect of cadmium on the liver or whether they are merely secondary to cadmium-induced pulmonary edema is not known. Changes in liver function in humans after long-term exposures have not been extensively examined.[1]

Changes in the activity of certain hepatic enzymes were noted in rats receiving 1 ppm cadmium in drinking water for 335 days; however, cadmium concentrations were not determined in the organs. In a similar experiment where rats received 0.5 ppm cadmium in drinking water for 1 year, the mean cadmium concentration in the liver was found to be 1.1 ppm, which is of the same magnitude as the cadmium concentration found in the liver of normal human adults.[1]

8.1.2.3 *Bone Effects*—Cadmium is not known to be concentrated in bone tissue; thus, any direct action upon bone is unlikely.[1] Some instances of pseudo-fractures have been reported among cadmium workers; however, the effects on bone are probably secondary to the effects on calcium-phosphorous metabolism. It

is thought that chronic cadmium poisoning in conjunction with a calcium and vitamin D deficiency causes the Itai-itai disease, a bone malady occurring in Japan.[1] This disease is a form of osteomalacia afflicting mainly post-menopausal Japanese women living in Toyama Prefecture. The disease is characterized symptomatically by lower back and leg pains. Chronic cadmium poisoning is thought to be one of the causative agents because a cadmium mine is located upriver from the endemic area. Analysis of food and water in the area, in combination with data on the average daily intake of different foods, led to an estimated daily ingested dose in recent years of 600 μg. Estimates for earlier years are not available.[1]

Animal studies have shown that exposure to cadmium in calcium-deficient rats will cause a rapid demineralization.[4] Further studies[5] revealed that rats exposed to 10 ppm of cadmium in drinking water and a low-calcium diet showed renal tubular damage as well as a significant reduction in the mineral content of bone. It is not known whether the bone changes were caused by changes in renal function or by an effect of cadmium on the intestinal absorption of calcium.

8.1.2.4 *Anemia*—Anemia has been observed in cadmium workers exposed to cadmium oxide dust or fumes. A significant correlation was found between high cadmium levels in blood and low hemoglobin levels.[1] Although the number of eosinophile cells increases, white cells are generally normal in exposed workers.[1]

Anemia has been frequently evident in experimental animals that were either orally or systematically exposed to cadmium.[1]

8.1.2.5 *Cardiovascular Disease and Hypertension*—Cadmium has been shown to cause hypertension in animals; furthermore, human beings with hypertension excreted more cadmium via urine and had a higher cadmium-to-zinc ratio in their kidneys than normotensive subjects. Carroll[6] found a correlation between the concentration of cadmium in the air of 28 American cities and death rates from hypertension and arteriosclerotic heart disease. Hickey et al.[7] made a similar study and found that cadmium together with vanadium was correlated with mortality from heart disease.

Hunt et al.[8] reanalyzed Carroll's data and found that there was a higher correlation between population density and death rates than between cadmium concentrations in air and death rates.

In *Cadmium in the Environment*[1] this question was discussed in detail and it was stated: "The results from epidemiological studies are hitherto ambiguous. They have been obtained by associating cardiovascular disease with dustfall data or cadmium concentrations in air. Other more important sources of cadmium exposure have not been considered." In addition to the earlier mentioned effect of population density, it was pointed out that smoking had not been considered as a variable in Carroll's analysis. Furthermore, a higher prevalence of hypertension has not been found among workers exposed to cadmium or in populations in Japan exposed to cadmium via food.

Hammer et al.[9] studied groups of workers with low, intermediate, and high exposure to cadmium. They could not find a consistent relationship between cadmium and blood pressure. Evidence is still lacking for associating hypertension with cadmium exposure.

8.1.2.6 *Gonadal Effects*—Systemic administration of cadmium has caused acute testicular necrosis in a number of animal species. Although high concentrations of cadmium have been found in testicular tissue from occupationally exposed men, acute testicular necrosis from exposure to cadmium has not been reported in humans. The effects of cadmium on testes and ovaries of humans have not been studied extensively. The repeated, demonstrated effects of cadmium on animal gonads emphasize the need for further study.[1]

8.1.2.7 *Carcinogenesis*—Studies in rats have shown that cadmium injected subcutaneously or intramuscularly has resulted in sarcomas (solid tumors) at the injection site.[1]

The evidence that cadmium may act as a carcinogen in man is not conclusive.[1] One report on the prevalence of cancer among workers exposed to cadmium oxide dust in the production of alkaline batteries

showed that 8 of 74 men with at least 10 years exposure had died. Of the eight, three had died of cancer of the prostate.[1] Another report on 248 workers exposed for a minimum of 1 year to cadmium oxide showed that four had developed cancer of the prostate.[3] According to annual incidence rates supplied by the regional cancer registry, the expected number of cases of prostatic cancer was 0.58.[1] Further studies are needed to obtain conclusive evidence of carcinogenesis associated with cadmium in humans.

The possible association between cadmium and cancer of the gastrointestinal tract has not been studied extensively.

8.1.2.8 *Teratology*—Data dealing with the teratogenic effects of cadmium in humans are lacking. One study indicates a significant decrease in weight in newborn children of cadmium-exposed women.[1]

8.1.2.9 *Mutagenesis*—Very little information is available concerning possible genetic effects of cadmium and cadmium compounds.

8.1.2.10 *Summary*

- Based on animal experiments, three clearly demarcated stages result from the inhalation of cadmium oxide or cadmium chloride aerosols. Only the first two of these have been found in man.
- Emphysema of the lung was found among male workers chronically exposed to cadmium oxide dust. Exposure levels were in the 3- to 15-mg/m^3 range.
- Determination of dose-response relationship is not possible at the present time because of the absence of data.
- In fatal cases of acute cadmium poisoning by inhalation, pathological changes have been found in the kidneys.
- Proteinuria is the most common clinical manifestation of renal damage.
- A concentration of approximately 200 ppm (wet weight) in the renal cortex may cause the appearance of tubular dysfunction in sensitive individuals.
- Microscopic changes may appear in the liver as a result of acute exposure to cadmium oxide fumes.
- Cadmium effects on bone do not appear to be direct but are probably secondary, reflecting defects upon calcium metabolism.
- A significant correlation seems to exist between high cadmium levels in the blood and low levels of hemoglobin.
- Further evidence is necessary before hypertension in humans can be linked with cadmium in the body.
- To definitively associate cadmium with carcinogenesis, further studies are necessary.
- Data dealing with teratogenic and mutagenic effects of cadmium are lacking.

8.1.3 Clinical Studies

8.1.3.4 *Itai-itai Disease, Proteinuria, and Cadmium Exposure — The Japanese Experience*—The so-called Itai-itai disease was first seen in villages along the Jintsu River in Toyama Prefecture, Japan. This is a bone disease, osteomalacia, that mainly affects women above 40 years of age who have had multiple pregnancies.

The cause of this disease is thought to be long-term ingestion of rice contaminated by cadmium from river water used in irrigating rice fields.

In *Cadmium in the Environment*,[1] this disease is discussed in detail. The authors concluded that "The Itai-itai disease is a manifestation of chronic cadmium poisoning. It might well be, however, that cadmium has acted upon a population particularly sensitive because of deficient consumption of certain essential food ingredients and vitamins. A low intake of calcium and vitamin D may have been of particular importance."

Epidemiological studies in the Toyama area showed that in the endemic district about 50 percent or more of the inhabitants older than 60 had proteinuria. A high prevalence of proteinuria also occurred in males; however, males generally did not show signs of Itai-itai disease. The proteinuria was of the tubular type seen in chronic cadmium poisoning. A higher prevalence of glycosuria was also found in the endemic area.[1]

The findings in Toyama initiated studies in other areas of Japan where high concentrations of cadmium had been found in rice such as in a polluted area on Tsushima Island.[1] Itai-itai disease was not found, but a higher prevalence of proteinuria was discovered among both males and females living in the most polluted area compared with a control area. It was concluded that the data from Tsushima Island strongly supported the hypothesis that cadmium intoxication might have occurred in parts of Japan other than Toyama.

During the past few years several areas have been under study for the effects of cadmium pollution. The main aim has been to find cases of Itai-itai disease, but as the screening methods for detection of this disease include tests for proteinuria, some data can be used for epidemiological evaluations. A comprehensive review of the recent experience includes descriptions of the methods used, the areas under study, the exposure conditions, etc.[10]

At present, data are available from Fuchu (Toyama Prefecture), Tsushima (Nagasaki Prefecture), Bandai (Fukushima Prefecture), Annaka (Gumma Prefecture), Ikuno (Hyogo Prefecture), Kakehashi (Ishikawa Prefecture), and Omuta (Fukuoka Prefecture) and from areas in Akita, Miyagi, and Oita Prefectures.[10]

In most areas, several thousands of women above 30 or 40 years of age living in both polluted and control areas have been examined for proteinuria. Testing has usually been by using trichlorouric acid or sulfosalicylic acid. Although the standard screening method set criteria for evaluating proteinuria, very few of the published studies give detailed ratings. A careful examination of the procedures has shown that in many instances only + has been used and that in some areas a + outfall of the test has been recorded as positive, whereas in other investigations a + result has been recorded as negative.[10] This inconsistency makes it difficult to compare different areas. Moreover, the investigations have not been performed on a blind basis. It has not always been possible to obtain age-related prevalences of proteinuria in both exposed and control areas. Furthermore, at least one control area (in Annaka) is not a true control area because the concentrations of cadmium in rice were about the same as in the polluted area. In other control areas, it has not always been possible to estimate the exposure because cadmium has not been estimated in the rice.[10]

Despite many difficulties in interpreting the results from the recent investigations in Japan, the following findings are worth mentioning. In Ikuno, 1700 women over 30 years of age were examined in 1971 in the polluted area where average cadmium concentrations in rice were 0.56 ppm in 1970 and 0.39 ppm in 1971. The prevalence of proteinuria was 58 percent, compared with 33 percent in a control area. In two other control areas investigated in 1972, the prevalence of proteinuria was 4 and 9 percent. In Kanahira, Kakehashi, where the average cadmium concentration in rice was 0.8 ppm, the prevalence of proteinuria was 39 percent, as compared with 22 to 30 percent in three villages with average rice concentrations of 0.23 to 0.34 ppm.[10]

In Gumma, age-related prevalences could be calculated, but since the exposure in the "control area" was probably about the same as in the polluted area, the results from this study can thus not be used. In both areas there was a sharp increase in proteinuria with age.

Earlier findings in Fuchu (Itai-itai area) have been confirmed, whereas recent investigations on Tsushima Island in 1971 and 1972 have not confirmed the earlier mentioned findings in the polluted area. In these later studies, however, one control area was omitted in 1971, and in 1972 no control area was included, which makes it difficult to compare the studies.[10]

There are many inconsistencies and errors in the epidemiological methods. A great need exists for more carefully designed epidemiological studies in Japan. The present data, however, indicate that in areas with excessive exposure to cadmium, the prevalence of proteinuria seems to be higher than in the areas with lower exposures. Although the evidence is not conclusive, it points to cadmium toxicity as the cause of Itai-itai disease.

8.2 ECOLOGICAL IMPACT

Studies that deal with the concentrations of cadmium in aquatic and terrestrial ecosystems and the effects of the concentrations upon these ecosystems are limited in number.

The chief concerns regarding cadmium in these ecosystems are the possibility of its movement through food chains to humans and its possible detrimental effects upon plants and animals within the ecosystems.

Cadmium is usually present in the environment in small amounts and is usually associated with zinc.[11] Zinc is considered to be an essential element for both plants and animals[12] and is translocated from the soil through various food chains. Under normal circumstances, the level of cadmium in the environment is determined by the geochemical composition of the region and is not high enough to adversely affect the health of the indigenous plant or animal populations. Ecological dangers from cadmium exposure, therefore, arise from activities associated with the production and use of the metal.

The large variety of sources from which cadmium may enter the environment are discussed in Section 5 of this report. Concentrations of cadmium in various substances and plants or animals are listed in Table 8.2.

Table 8.2. CONCENTRATION OF CADMIUM IN VARIOUS SUBSTANCES[11]
(ppm of dry plant and animal tissue)

Abiotic components		Marine and land plants		Animals	
Substance	Concentration	Substance	Concentration	Substance	Concentration
Igneous rock	0.2	Plankton	0.4	Coelenterata	1
Shales	0.3	Brown algae	0.4	Annelida	--
Sandstones	0.05	Bryophytes	0.1	Mollusca	3
Limestones	0.035	Ferns	0.5	Enchinodermata	1
Soils	0.06	Gymnosperms	0.24	Crustacea	0.15
Fresh water	0.08	Angiosperms	0.64	Insecta	--
Sea water	0.00011	Bacteria	--	Pisces	3
		Fungi	4.0	Mammalia	--

The possible avenues of environmental transport of cadmium are shown in Figure 8.1. The term "biota" refers to all living organisms, including humans. Biological organisms may be affected by cadmium intake at any of the points listed.

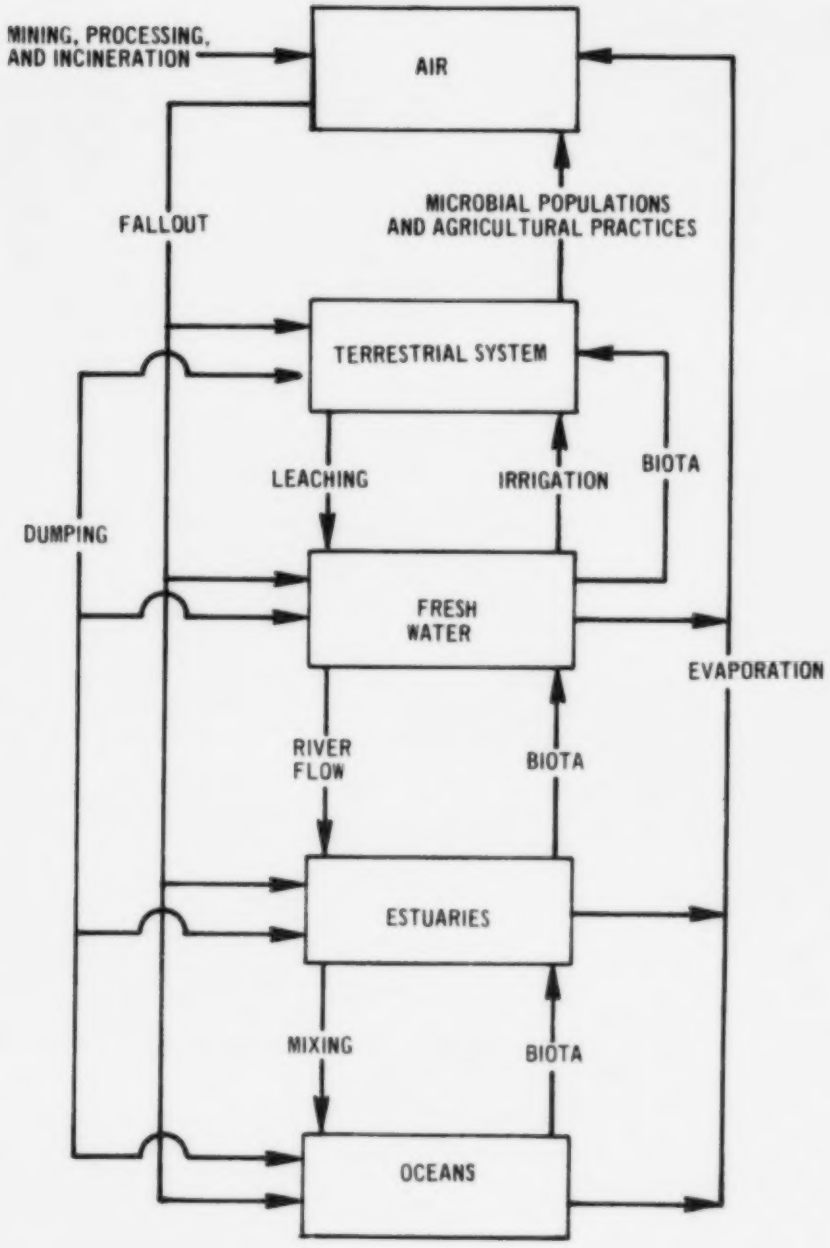

Figure 8.1. Environmental transport of cadmium.

Studies and surveys in areas surrounding smelters have shown decreasing concentrations of zinc and cadmium in the soil, as well as in plants and animals, with increasing distances from the source.[13,14] Leafy crops show higher levels of cadmium than root crops, probably because of direct deposition.

A study conducted by Dorn et al.[13] on lead mining in Missouri points out the levels of cadmium, copper, lead, and zinc that may be added to naturally occurring levels of these elements in soil and vegetation by mining processes. Two farm sites were selected for study: one approximately 0.8 km and the other 26 km from the smelter stack. Soil and vegetation and hair, blood, and milk from cows were collected from each farm at three time periods during 1 year. Statistically significant differences in cadmium levels were observed between farm sites for the following variables: soil, roots of vegetation, leaves of vegetation, and hair collected from cows. The levels of cadmium in milk never exceeded 0.5 μg per 100 ml. There was no significant difference in cadmium concentrations in milk between the farm sites, which would seem to indicate that cadmium is not readily assimilated and/or secreted in milk of cows. Vegetation levels were reported to be between 3 and 10 μg/g of dry weight. Exposure longer than 1 year to the same levels of cadmium in vegetation as these would probably result in higher levels in milk than reported here, however.

Smith and Huckabee[14] report that Munshower in his studies in Deer Lodge Valley in Southern Montana, an area near a smelter, found soil concentration factors were: 1 for grasses, 2 for forbs, and 1.5 to 3.0 for insects; however, concentration factors varied considerably with species. The same study noted an increase in the concentration of cadmium in the kidney and liver with increasing age in the cattle in the area.

Cadmium is added to the soil through deposition from the air and through addition of fertilizers and pesticides. The airborne forms of cadmium also fall on growing vegetation through precipitation and dustfall.

The uptake of cadmium by oats was studied by John et al.[15] The cadmium content of the soil was shown to markedly affect the cadmium content of the roots. Cadmium was translocated to the tops to a lesser extent. The type of soil appeared to affect the movement of cadmium into the shoots. Oat shoots grown in Richmond soil with 46.4 ppm of cadmium contained 16.1 ppm as compared with 0.51 ppm in shoots grown in soil with cadmium levels of 1.3 ppm. Cadmium levels were measured using nitric acid extraction.

In another study, John et al.[16] noted that the cadmium content of the plants appeared to be related to the amounts of exchangeable cadmium in the soil rather than to the total cadmium present in the soil. The higher levels of cadmium were associated with increased soil acidity.

Lagerwerff[17] observed that large changes in the cadmium content of the soil caused only small increases in the cadmium content of radish tops; a five-fold increase in the soil resulted in a two-fold increase in the tops. The cadmium uptake in radishes was greater in soil with a pH of 5.9 than in soil with a pH of 7.2. Also, when plants were grown near a cadmium source, the aerial deposition accounted for more than 40 percent of the contents of the tops.

Schroeder and Balassa[18] reported cadmium uptake by 10 garden vegetables; in some, uptake was only by the roots and in others by the entire plant.

The availability of cadmium to plants is undoubtedly associated with microbial metabolism. Although the microbial metabolism of zinc has been rather thoroughly studied,[12] that of cadmium has not. Sulfate-reducing microorganisms are known to have produced sphalerite from zinc metal and zinc carbonate.[12] Sphalerite ores are a common source of both zinc and cadmium. Zinc carbonate (smithsonite) occurs naturally, although zinc metal does not. Sulfate-reducing microorganisms are also capable of reducing cadmium carbonate to cadmium sulfate.[19]

Cadmium behaves differently when in the presence of zinc than when alone. Zinc is a cofactor for many enzymes and without it the enzymes do not function. Cadmium can replace zinc as a cofactor and thereby cause many of the enzymes to cease functioning.[14] The presence of zinc in the soil changes cadmium

uptake in plants. At low concentrations of cadmium, zinc suppresses its uptake, but at high concentrations of cadmium the zinc increases uptake.[14]

Lichens, mosses, leaf litter, and humus tend to accumulate metals deposited on their surfaces.[20] The metals do not appear to penetrate the plant as long as a cuticle is present. In mosses they tend to accumulate because of ion exchange.

Accumulations of metals in leaf litter may be the most serious effect of metal deposition. The effect of cadmium and other metals on the organisms that decompose leaf litter is not known; however, the blocking of negatively charged organic groups by metal ions would decrease the probability of litter decomposition.

Extremely high levels of metals would be required to prevent litter decomposition. The effect of the metals on the microorganisms that bring about litter decay is not known, but the decomposition of litter is an integral part of mineral turnover and biogeochemical cycling. Any interference with this cycling will produce a profound effect upon terrestrial ecosystems.

The discharge of cadmium into ocean and fresh water streams results in an increase in the cadmium levels in the organisms living in these waters.[14,21] Both marine and fresh water animals are capable of concentrating cadmium.[14,21] however, the effects of cadmium at sublethel levels on the organisms themselves are not known.

Present knowledge concerning the ecological effects of cadmium can be summarized as follows:

- Data dealing with the effects of cadmium in terrestrial and aquatic ecosystems are limited.
- Under normal circumstances the level of cadmium in the environment is insufficient to adversely affect the health of the indigenous plant and animal populations.
- Organisms living in the proximity of cadmium sources have higher levels of cadmium within their bodies than those in non-contaminated areas.
- Leafy crops show higher levels of cadmium than root crops, probably because of direct deposition.
- The amount of uptake of cadmium from the soil is determined by soil type, pH, amount of exchangeable cadmium, and microorganismal activity. The amount of zinc in the soil also influences cadmium uptake.
- Lichens and mosses tend to accumulate metals deposited on their surfaces. The accumulation results from ion exchange. The metals do not appear to penetrate the plant as long as an intact cuticle is present.
- The accumulation of cadmium and other metals in the leaf litter and humus may be the most serious aspect of metal deposition. The effect of metal deposition on litter decomposition and biogeochemical cycling is not known.

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9. CONTROL TECHNOLOGY

9.1 AIRBORNE EMISSIONS

Cadmium emitted into the atmosphere will generally be in the form of particulate matter usually as the oxide, but also as the sulfide or sulfate. Because the boiling point of cadmium is fairly low, 767°C (1410°F), the metal may be vaporized in high-temperature processes and condensed into particles as the process off-gases are cooled. This method of formation would result in very fine particles in the micrometer and submicrometer range.

The exact size distribution of cadmium-containing particles from these various processes has, unfortunately, not been clearly defined. The limited information available indicates that 40 percent of the particulate mass may be smaller than 2 micrometers in diameter. In processes where a large fraction of the cadmium-containing particulate is formed by the vaporization/condensation method, it is possible that a significant amount of cadmium may be contained in particulate matter even smaller than 0.1 micrometer. The shape of the condensed particles is not known, either, although there are indications that the particles might not always be spherical. There is evidence that the percentage concentration of cadmium in fly ash is higher in the finer particles than in the coarser particles.

It is evident, therefore, that the control of atmospheric cadmium emissions requires the ability to capture fine particles.

9.2 WATERBORNE EMISSIONS

Waterborne cadmium emissions are generally in the form of suspended particulates, although cadmium may sometimes be present in a soluble form such as cadmium sulfate. These aqueous emissions may result directly from various processing steps involving cadmium (such as the aqueous beneficiation of zinc ores or the spills, washdowns, and rinsings from cadmium electroplating operations) or they may result from leaching and washing of smelter slag heaps by rainwater.

9.3 CONTROL METHODS

9.3.1 Control of Airborne Cadmium Emissions

The technology currently employed to control cadmium emissions is directed toward control of particulate matter in the micrometer range. The devices most frequently used are fabric filters and electrostatic precipitators. Scrubbers are also utilized, but less often, possibly because many sources of cadmium emissions must keep the particles dry for purposes of recycle to the process. Cyclones, which are not efficient in collecting fine material, can be employed only to remove the coarser particulate matter upstream of one of the other devices.

Reasonably high removal efficiencies for fine particulate matter in the range of 0.2 to 1.0 micrometer are possible using existing devices, either alone or in combination, but only if these devices are large enough, installed in sufficient number, supplied with adequate energy, and operated correctly. The economics of installing the equipment required to provide removals higher than those currently achieved by cadmium emitters, will thus be unfavorable at best, and possibly prohibitive, depending upon what degree of

additional removal is desired. Research programs currently underway within EPA are intended to make greater control of fine particles feasible by improving the efficiency of control techniques in the submicrometer range at a limited increase, or possibly even at a decrease, in system cost.

Capital costs of completely installed, high-efficiency particulate collection systems vary from about $4 to $12 per actual cubic foot per minute (acfm) of gas treated and are highly dependent on the nature of the source, the efficiency required, and the size of the unit. Complete operating costs, including amortization, depreciation, and maintenance can vary from about $0.50 to $5.00/acfm-year. The selection of the most economical device in any one particular case depends on many factors.

If, indeed, a significant fraction of cadmium emissions consists of particles smaller than 0.1 micrometer, then the technology for controlling this fraction of the emissions may not exist at the present time.

9.3.1.1 *Fabric Filters*[1]—Fabric filters, or baghouses, are currently employed to control many cadmium emission sources. This technique involves passage of the particle-containing gas stream through a porous filter medium consisting of woven or fibrous fabric. The fabric may be wood or cotton, or—for higher temperature and more corrosive environments—may be Dacron, Teflon, glass, or any of a number of other materials. The collected particles form a cake on the filter, which must be removed periodically.

Particles are collected via several mechanisms in bag filters. The most important are:

- Direct interception of a particle by the filter (or, more accurately, by the cake of collected particles built up on the filter) as the particle is carried by the gas stream.
- Inertial impaction, in which the momentum of entrained particles causes them to leave the gas stream and to collide with the filter.
- Brownian diffusion of fine particles, causing diffusion of these particles to the surface of the filter.

Fabric filters are efficient for removing fine particles in the micrometer range. There are indications that—if the appropriate fabric is selected, if the air/cloth ratio (i.e., the gas velocity) is held sufficiently low, and if the entire baghouse system is correctly built and maintained leak-free—the fraction collection efficiency of particles 1.0 micrometer in size may be as high as 99 percent. Filters employed by some of the emitters of cadmium do not appear to be designed or operated to achieve such high efficiencies. Although a correctly operated baghouse without imperfections in the filters can be efficient, in practice a large number of filters are often not in correct working order throughout the entire operating period. Thus collection efficiencies below the design efficiency are quite possible during operation.

Most fabric filter bags cannot be operated above 284°C (550°F); for this temperature, a glass fabric is required. This temperature limitation does not appear to be a severe problem in many of the high-temperature processes emitting cadmium; the process off-gases must be cooled before entering the filter anyway because the filter is frequently followed by a scrubber for SO_2 removal. The concentrations of SO_2 expected (e.g., in off-gases from smelter operations) are not believed to pose a serious problem for filters, so long as an appropriate fabric is selected.

In summary, the advantages of fabric filtration as a technique for controlling cadmium emissions are:

- Filters can be very efficient in removing fine particles on the order of 1.0 micrometer, and possibly smaller.
- Disturbances in the process operation would not affect filter performance.

The disadvantages of filters are:

- Low air/cloth ratios are required in order to reduce the pressure drop and to maintain high efficiencies (i.e., the baghouse must be large).

- Pressure drop across the filter is high relative to electrostatic precipitators, although low in comparison with high-energy scrubbers.

- Maintenance requirements are high for correct operation.

- Temperature limitation of fabric filters may limit application in some cases and could result in filter damage in the event of a temperature excursion.

- Fabric filters would be blinded if the particles were sticky (although this should not be a problem for most cadmium emission sources).

- The efficiency of fabric filters on particles below 0.1 micrometer is not clear.

9.3.1.2 *Electrostatic Precipitators*[2] Precipitators, along with fabric filters, are perhaps the most commonly employed devices for removing cadmium-containing particles from process off-gases. This technique involves: (1) production of an electric charge on the particles in the gas stream, (2) attraction of the charged particles toward oppositely charged plates placed in the gas stream and precipitation of the particles onto the plates, and (3) removal of the collected material from the plates.

Precipitators can be fairly efficient in removing fine particles, but not as efficient as fabric filters. Fine particles are more difficult to charge than coarser ones; moreover, the fine material migrates more slowly to the collection plates, thus necessitating a large plate area. For these reasons, the capital cost of a precipitator increases exponentially with increasing collection efficiencies. Some precipitators have been reported to be 98 percent efficient in collecting particles of 1.0 micrometer in diameter. It is not apparent, however, that such high efficiencies on fine particulate matter are frequently attained with precipitators employed by cadmium emission sources.

A problem encountered in precipitation of cadmium-containing particles is the high resistivity of the particles. Moisture conditioning of the inlet gas to the precipitator may be required for efficient removals.

Like filters, precipitators are limited by a maximum operating temperature. For precipitators, this limit is currently about 425°C (800°F). Although it is sometimes advantageous to operate a precipitator near the maximum temperature, most sources of cadmium emissions should find little difficulty in operating at temperatures well below the maximum.

The concentration of SO_2 (and SO_3) expected (for example, in the off-gases from smelter operations) should, if anything, aid precipitator performance.

The advantages of precipitators for controlling cadmium emissions are:

- Precipitators can be relatively efficient in removing fine particles in the micrometer range.

- Precipitators give very little pressure drop, with the result that power consumption is low compared to other control devices offering the same removal efficiencies.

The disadvantages are:

- Precipitators must be large, because of the low gas velocities required to maintain high collection efficiencies and to prevent reentrainment of collected particles.

- The efficiency of precipitators on particles smaller than 0.1 micrometer is not known.

- The small size and high resistivity of cadmium-containing particles make them difficult to charge.

9.3.1.3 *Scrubbers*[3] – Scrubbers are not used as widely for the control of cadmium emissions as are filters and precipitators. One reason for their more limited application may be that in smelters—the most significant sources of cadmium emissions—the collected particulates must be dry so that they can be recycled to the process. With the advent of high-energy, high-efficiency scrubbers, however, these devices may find increased application in situations where simultaneous removal of particulates and of SO_2 is desired.

Scrubbers are available in a number of different designs, but are generally based upon the principle of impaction of water droplets against the entrained particles. Scrubbers operating with a very high energy input to the water or the gas streams—i.e., scrubbers operating with a pressure drop on the order of 40 to 100 inches of water—provide significant removal efficiencies in the submicrometer range. For example, some experience indicates that such high-energy scrubbers may be approximately 99 percent efficient in removing particles of 1.0 micrometer.

Scrubber efficiency can be improved in general by increasing the energy input to the devices. Currently available high-energy scrubbers supply this energy to the water and gas streams in such a manner that particle collection by the impaction mechanism is increased. It appears, however, that high efficiency in control of fine particulate matter may be achieved more effectively and more economically if the scrubbers are designed so that mechanisms in addition to impaction are brought into play—such as diffusiophoresis, thermophoresis, and condensation effects. Scrubbers incorporating these effects—including condensation scrubbers and charged droplet scrubbers—are still in the development stage.

The advantages of scrubbers are:

- Small size relative to competing devices.
- High efficiency in removing particles in the micrometer range.
- Potential for simultaneous removal of particulate matter and gaseous pollutants.

The disadvantages of scrubbers are:

- They give a slurry by-product. Consequently, they would complicate recycling the solids to the process if the scrubber system were used as the primary control technique, and they would necessitate a settling pond or equivalent means for removing the suspended particulate matter. A contaminated water disposal problem may result.
- The efficiency of scrubbers on particles smaller than 0.1 micrometer is not known.

9.3.2 Control of Waterborne Cadmium Emissions

If the cadmium is present in the form of suspended particulate, the aqueous emissions that result directly from process operations involving cadmium may be controlled by employing settling ponds or thickeners. Filtering or centrifuging the aqueous wastes might also be considered.

If the cadmium is present as a soluble compound, it might be removed by precipitation, followed by removal of the resulting solids. Alternatively, the techniques of ion exchange, solvent extraction, or electrolytic deposition might be employed.

9.4 REFERENCES FOR SECTION 9.

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